

**PYROLYSIS OF ORGANIC  
MOLECULES WITH APPLICATIONS  
TO HEALTH AND ENVIRONMENT**

**28**

**S.C. MOLDOVEANU**

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# PYROLYSIS OF ORGANIC MOLECULES WITH APPLICATIONS TO HEALTH AND ENVIRONMENTAL ISSUES

by

**Serban C. Moldoveanu**

*R.J. Reynolds Tobacco Co.  
950 Reynolds Boulevard  
Winston-Salem, NC 27105, USA*



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## PREFACE

The present book is a continuation of two other volumes published in the series *Techniques and Instrumentation in Analytical Chemistry*. The first volume, *Analytical Pyrolysis of Natural Organic Polymers*, presents results on pyrolysis for natural polymeric materials such as cellulose, starch, lignin, proteins, various organic geopolymers, and complex materials such as plant parts and microorganisms. The second volume, *Analytical Pyrolysis of Synthetic Organic Polymers*, describes the pyrolysis of plastics, fibers, elastomers, adhesives, coatings, etc.

The study of pyrolysis of non-polymeric organic molecules is the next logical subject related to pyrolysis. However, besides describing the pyrolysis results for various classes of compounds, the focus of the presentation needed a change compared to that of the previous two books. While pyrolysis of polymers has important analytical applications, for smaller molecules this use is very limited. On the other hand, the impact on environmental and health issues of pyrolysis of non-polymeric molecules is very important. Numerous human activities such as fuel burning, waste incineration, and industrial pyrolysis processes applied for synthetic purposes generate many compounds that may have adverse effects on health and environment. It is sufficient to indicate that main sources of polycyclic aromatic hydrocarbons (PAHs), halogenated dibenzodioxins (dioxins), halogenated dibenzofurans (furans), and heterocyclic amines are related to the pyrolysis of non-polymeric molecules. For this reason, the present book discusses the results of pyrolysis for different classes of non-polymeric organic molecules from the point of view of potential formation of noxious compounds.

The book is organized in three parts. The first part presents the basic concepts related to pyrolysis and to risk assessment and toxicology. It presents the main chemical reactions encountered during the pyrolytic processes, aspects of physicochemistry of thermal degradation, and basic instrumentation used in analytical pyrolysis.

The second part is the core of the book. In this part, the main results published in the literature regarding the pyrolysis of various classes of organic compounds are presented in a systematic manner. Some unpublished original results using pyrolysis coupled with gas chromatography/mass spectrometry (Py-GC/MS) also are included in this part. The compounds are classified based on their chemical structure, each class being presented in a separate chapter. Typical reactions taking place under the influence of heat are described for each class and exemplified for specific molecules. Particular attention is given to reactions that generate harmful compounds.

The third part of the book provides information on toxicological aspects of a few selected classes of compounds that are considered the most damaging to the environment and human health and that are generated in pyrolytic processes. Among these compounds are polycyclic aromatic hydrocarbons, halogenated dioxins and dibenzofurans, and heterocyclic amines.

In the writing of this material, the author received substantial help from Dr. Suzana Theophilus, particularly regarding the toxicological properties of different components in pyrolysates. Also, Dr. Charles Risner and Dr. Niraj Kulshreshtha reviewed several chapters of the book and made valuable corrections to the text. Mrs. Carol Moldoveanu had considerable contribution in editing and correcting the entire manuscript.

## CHAPTER 1

*Introduction***1.1. PRELIMINARY INFORMATION ON PYROLYSIS*****General aspects***

Heating of an organic compound beyond a certain temperature leads to its decomposition since its chemical bonds have a limited thermal stability. This type of decomposition usually leads to the formation of smaller molecules, although the resulting fragments may interact and further generate larger compounds compared to the starting molecule. When the heating temperature is above 300–350 °C, the chemical processes caused by the thermal energy alone are called pyrolysis (Py) [1–4]. Chemical reactions caused by heat alone at lower temperatures (e.g., 175–250 °C) are thermal decompositions.

Pyrolysis is frequently associated with burning, although burning is more complex. The main process in burning is typically the combustion, although other processes including pyrolysis, volatilization, steam distillation, aerosol formation, etc., are present. Combustion is an oxidation process (commonly using oxygen), which produces heat and usually generates very small molecules, such as H<sub>2</sub>O, CO, CO<sub>2</sub>, and N<sub>2</sub>, from organic compounds [5]. In the areas close to the burning zone, where heat is generated, materials may undergo pyrolytic processes leading to thermal decomposition products. A mixture of pyrolysis products, combustion products, and part of the intact initial material may result from burning. The initiation of burning is caused in many cases by a pyrolysis process. For these reasons, pyrolysis and burning are closely related subjects, and pyrolysis can be studied either in an inert atmosphere or in the presence of a specific level of oxygen mixed in an inert gas.

The term pyrolysis is not restricted to the decomposition of pure compounds. The same term can be used in connection with the thermal decomposition of mixtures or of complex materials. Pyrolysis can be applied to solid, liquid, and gaseous substances.

Although pyrolysis is simpler than burning, it is common that the pyrolysis products (i.e., pyrolysates) of organic compounds consist of complex mixtures. Depending on the pyrolysis conditions, the constituents of pyrolysates may result from the initial material that undergoes pyrolysis, and may also result from further decomposition of fragments of the initial material or from subsequent reactions of the pyrolysate components. In most cases, pyrolysate constituents are smaller molecules than the initial ones that were subjected to pyrolysis. However, in some cases, pyrolysate constituents are larger molecules than the initial ones. For example, many pyrolytic processes generate char in addition to other products. Char is a complex material containing graphite-like moieties, which may contain various other organic groups depending on the initial molecule that is pyrolyzed. Char can be considered to have a polymeric structure [6].

In most cases, experimental pyrolysis is conducted without the influence of additional compounds. However, in some cases, a given method can be adapted for a specific experimental purpose to include additives, such as reagents or catalysts. For example, in some cases a reducing reagent like hydrogen or an oxidant like oxygen may be added during the pyrolytic process. In this type of pyrolysis, the decomposition of the sample still should be caused by the heat alone, and the reagent should react only with the pyrolysis products to generate new compounds. However, this is not always possible, and the addition of a reagent gas such as hydrogen or oxygen may be necessary and may lead to additional reactions with the initial pyrolyzed material. With addition of oxygen, pyrolysis instrumentation can be used to simulate burning.

Besides reagents, pyrolysis methods can sometimes intentionally employ a catalyst. The decomposition products that are generated due to heat further react in the presence of the catalyst to form new compounds. Both reagents and catalysts can be combined (i.e., used at the same time) for specific experimental purposes related to pyrolysis [7,8].

### ***The purpose of experimental pyrolysis***

Pyrolysis (or pyrolysis associated with burning) occurs in various types of processes such as burning of waste materials, incomplete combustion of fuels, or unintentional fires (such as forest fires). Experimental pyrolysis performed in laboratories may be used for different purposes. For example, pyrolysis can be conducted for simulating and studying pyrolytic processes that occur during burning or for analytical or synthetic purposes.

Pyrolysis can be conducted with the purpose of synthesis at laboratory scale and is also used in important industrial processes, such as those involved in petroleum refining, acetylene synthesis, coal pyrolysis, or pyrolysis of biomass. These types of processes will be discussed in this book, but only from the basic chemistry point of view, excluding technological details.

Analytical pyrolysis is applied to the characterization of different materials, first, by exposing them to pyrolysis and, second, by analyzing the resultant pyrolytic products. The technique can be used, for example, for the measurement (in different matrices) of the initial compound that was pyrolyzed. However, its utility is not limited to this type of application. The technique is frequently used for the study of the pyrolytic process and for the characterization of the chemical composition of the pyrolysates generated from different substances or processes. The term analytical pyrolysis will be used in this book in its broader sense (i.e., not limited strictly to pyrolysis conducted for the analytical measurement of an initial compound).

Analytical pyrolysis is well suited for the analysis of polymers. Since some natural and synthetic polymers are not easy to analyze directly, their identification can be performed more easily using pyrolysis methods. The subject of analytical pyrolysis of polymers has been thoroughly presented in several books [6,9], and the subject is beyond the purpose of the present material.

Analytical pyrolysis of non-polymeric organic molecules is not utilized so frequently for the measurement of the initial pyrolyzed compound because simpler and better analytical techniques typically are available for this purpose. However, analytical pyrolysis is still very useful in applications geared toward obtaining knowledge of the composition of pyrolysates and in the study of large-scale pyrolytic processes of non-polymeric molecules.

There are several ways of heating the sample during experimental pyrolysis. Analytical pyrolysis is conducted typically in "flash" mode, which involves the process of rapidly heating a small sample. The rate of temperature increase can be of the order of 10 °C/ms. After the desired pyrolysis temperature has been attained, the temperature is maintained practically constant (i.e., isothermal pyrolysis). In analytical pyrolysis, the sample size is typically between 0.1 mg and 2 mg. There are numerous analytical techniques associated with pyrolysis; these are typically designated in the scientific literature with a hyphen, followed by the additional technique name. One such technique, which is used most commonly, is gas chromatography (GC); the resulting technique, when combined with pyrolysis, is known as pyrolysis-GC (Py-GC). In this technique, the volatile pyrolysates are introduced directly into a gas chromatograph for separation and detection (a volatile pyrolysate is that portion of the pyrolysate that has adequate vapor pressure to be transferred to the gas chromatograph). Another common analytical technique is pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). In this technique the volatile pyrolysates are separated and analyzed by online gas chromatography/mass spectrometry. Infrared (IR) analysis can be used in a similar way in another technique called pyrolysis-gas chromatography/infrared spectroscopy (Py-GC/IR). The chromatographic separation sometimes can be excluded from the analytical process following pyrolysis. This is, for example, the case of pyrolysis-mass spectrometry (Py-MS), in which the volatile pyrolysates are detected and analyzed by online mass spectrometry.

Besides flash pyrolysis, other types of heating conditions during pyrolysis are used. One example is fractionated pyrolysis, in which the same sample is pyrolyzed at different temperatures for different times in order to study special fractions of the sample. A special type is stepwise pyrolysis, in which the sample temperature is raised stepwise and the pyrolysis products are analyzed between steps. Another special type is temperature-programmed pyrolysis, in which the sample is heated at a controlled rate within a temperature range. Larger laboratory scale pyrolysis followed by analysis of pyrolysates is also common. All these different heating conditions or amounts of initial sample are used, for example, for the purpose of evaluating the thermal properties of a specific material or for simulating the generation of pyrolysates under specific heating conditions. The fact that the pyrolysates are analyzed after the thermal decomposition step labels these types of studies as analytical pyrolysis studies, although they

are not usually performed with the purpose of identifying a starting material. Because of the versatility of analytical pyrolysis, a large number of the experimental results presented in this book and applied to non-polymeric organic molecules are related to this technique.

Regardless of the purpose of pyrolysis, the chemistry of the pyrolytic process and the study of the chemical composition of pyrolysates are important subjects. Since numerous pyrolysis products are generated in nature, the toxicological and environmental implications of the presence of pyrolysates are of considerable interest. Experimental pyrolysis of non-polymeric organic molecules focused on the composition of pyrolysates of different classes of organic compounds, and on their potential toxicity and environmental effects will be further elaborated in this book. The organic compounds discussed are classified based on their chemical structure. The first class is that of hydrocarbons, which are followed (in separate chapters) by compounds containing specific functional groups (halogenated compounds, alcohols and phenols, ethers, peroxides, carbonyl compounds, carbohydrates, organic acids, etc.). The nomenclature for the organic compounds discussed in the book is basically the one used in organic chemistry (with a systematic attempt to include IUPAC recommendations [10]).

Various aspects of pyrolysis and its use are discussed in a considerable number of publications. These include one journal dedicated solely to pyrolysis, *Journal of Analytical and Applied Pyrolysis*, many journals related to combustion such as *Fuel*, *Combustion and Flame*, *Proceedings of Combustion Institute*, etc., as well as a number of books and chapters covering this subject [1,6,9,11–21]. Part 2 of this book presents in a systematic manner the main results published in literature regarding the pyrolysis of non-polymeric organic molecules and also includes some unpublished original results obtained using pyrolysis coupled with gas chromatography/mass spectrometry on selected organic compounds.

## 1.2. PRELIMINARY INFORMATION ON RISK ASSESSMENT AND TOXICOLOGY

### **General aspects**

Various compounds generated by pyrolysis may present environmental or toxicological issues. Such issues, as they relate to specific classes of pyrolysis compounds, will be discussed in Part 3 of this book. In this section, some general aspects of risk assessment and toxicology will be outlined. Particularly, general information related to risk assessment will be discussed with the purpose of placing toxicology in the risk assessment context.

### **Risk assessment**

All human activities, products, and processes are associated with some degree of risk. An important part of risk assessment is related to the characterization of the risk associated with health hazards. The ultimate goal of risk assessment is to define and summarize all the relevant aspects of a potential risk in order to facilitate good risk management decisions.

Risk assessment takes into consideration a number of factors. These include the source of potential hazard, the chance of adverse effects occurring as a result of exposure to a potential hazard, the uncertainty associated with the occurrence of a specific adverse effect and its potential outcomes, the targets of interest, the time frame of the potential adverse effects, and the importance of the risk for the population for which the assessment is conducted. The results of risk assessment are then used by risk managers to make decisions.

There are several risk assessment models and several definitions for the terms involved, depending on the organization undertaking the risk assessment and the countries involved. However, the essential steps (after the identification and agreement regarding the issue at hand) are: (1) hazard identification, (2) dose–response assessment, (3) exposure assessment, and (4) risk characterization. These steps help to characterize risks in more elaborate terms than simply “safe/unsafe.”

### **Toxicology**

Toxicology is an important part of risk assessment, which comes into play mainly when dealing with steps 1 and 2 of the risk assessment process (hazard identification and dose–response assessment,

respectively). In its broadest sense, toxicology can be defined as the study of the toxic effects and mechanisms of action of an agent (e.g., a compound or a mixture of compounds) [22]. Toxicology, as an applied science, integrates knowledge regarding the toxicity of compounds gathered through either basic science (e.g., specifically designed experiments) or other scientifically established methods (e.g., data from an industry or government-sponsored project) for solving or preventing problems related to relevant human activities or issues of concern [23]. Basically, toxicology is a broad field, which deals mainly with the study of the adverse effects of chemicals on biological systems [23,24].

Pyrolysis of various substances or materials can generate compounds that may pose environmental and/or toxicological issues [25–27]. Descriptions of some health and environmental issues related to special classes of compounds generated by pyrolysis are discussed in Part 3 of this book.

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## CHAPTER 2

*The Chemistry of the Pyrolytic Process***2.1. BASIC CHARACTERISTICS OF PYROLYTIC REACTIONS*****General aspects***

The formation of pyrolysis products depends on the structure of the initial compound (parent compound) and also on pyrolysis conditions. When pyrolysis is performed intentionally, the conditions usually are selected to diminish the variability of the results and to simplify the pyrolysis outcome. Typically, this is achieved by selecting a precise temperature of pyrolysis and in some cases by performing pyrolysis in gas phase. In analytical pyrolysis, the process is commonly performed in an inert atmosphere. For synthesis purposes, the pyrolysis is also performed in a controlled atmosphere and very frequently in vacuum. Only during attempts to simulate a process such as burning, the pyrolysis is conducted in gases such as air or in mixtures of oxygen and nitrogen (or other inert gas) with a specific composition. When pyrolysis takes place unintentionally, these parameters (temperature, atmosphere, gas or solid phase) cannot be controlled.

Even in gas phase or in vacuum, the pyrolysis process can be more than the decomposition of one single molecular species, since the products of the initial decomposition may undergo further reactions under the influence of heat. Also, the initial process can be unique or more pyrolytic reactions occurring simultaneously can contribute to the generation of the pyrolysate. Particularly for pyrolysis in condensed phase, multiple chemical interactions occur. Even the cooling rate of the pyrolysate can influence the pyrolysis outcome. Addition of reagents and/or catalysts also influences (or determines) the pyrolysate composition. These factors, in addition to the multistep characteristics of pyrolysis, make the result of the pyrolytic process extremely complex.

In spite of the complexity of pyrolytic reactions, the pyrolysates are obtained by the cleavage of one or only a few bonds from the initial compound and of some of the initial pyrolysis fragments. Therefore, some resemblance between the initial molecule and the pyrolysis products is frequently obvious. For stable molecules, the decomposition typically requires a higher temperature, and the result consists of numerous fragments. When the generated fragments are very small, the connection with the parent molecule structure is more difficult to make.

The whole molecular structure as well as particular functional groups may contribute to the outcome of the pyrolysis. Due to many factors influencing the pyrolysis result, there are considerable differences in the pyrolysis outcome even within the same class of molecules. However, in molecules where a specific moiety is more susceptible to thermal decomposition, the members of a homolog series may have a similar behavior. As an example, pyrolytic decomposition of simple organic acids takes place mainly by the following reaction:



When a homolog series pyrolyzes similarly, the first members of the series sometimes may show peculiar properties. For example, formic acid decomposes like an acid, generating  $\text{CO}_2$  and  $\text{H}_2$ , but also as an aldehyde with the formation of  $\text{H}_2\text{O}$  and  $\text{CO}$ .

As the complexity of the whole molecule increases (addition of double bonds, aromatic rings, more than one functional group, etc.), the outcome of the pyrolysis depends more and more on the whole molecular structure, and the role of one single functional group becomes less important.

The decomposition mechanism plays a major role regarding pyrolysis outcome. For example, when the formation of free radicals occurs, the result is typically more complex than in cases when a concerted mechanism is responsible for the changes during pyrolysis. The individual reaction types taking place during pyrolysis can be studied independently. In the following sections, the most common

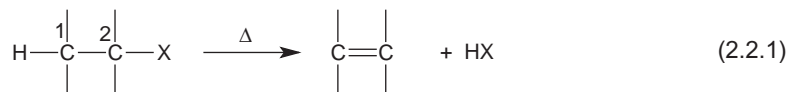
types of reactions encountered in pyrolysis will be presented and classified. These include elimination reactions ( $\alpha$ -eliminations,  $\beta$ -eliminations, 1,3-eliminations, and 1, $n$ -eliminations), fragmentation reactions (fragmentations, retro-ene reactions, retro-Diels–Alder and retro-aldol condensations, extrusions, etc.), rearrangements (1,2-migrations, rearrangements in compounds with bent bonds, electrocyclic rearrangements, sigmatropic rearrangements), other reaction types, and reactions in pyrolysis performed on purpose in the presence of reactants or catalysts. In many cases, more than one mechanism is needed to explain the variety of reaction products generated from the pyrolysis of one compound.

When mixtures of compounds are pyrolyzed, more than one molecular species is subject to thermal degradation. However, each component can be considered as starting the pyrolytic process independently, which reduces somewhat the complexity of the problem [1]. This does not exclude the further interaction of the molecular fragments resulting from independent pyrolysis processes. Depending on the particular molecules that are pyrolyzed, the pyrolysate contains a mixture of pyrolytic products of each component, with or without compounds generated from a combination of fragments from the initial components.

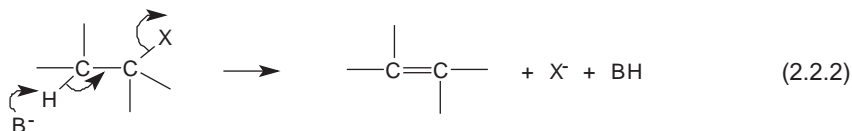
## 2.2. ELIMINATION REACTIONS

### General aspects

The pyrolytic elimination is a model reaction, which probably dominates most pyrolytic processes. A simple reaction of this type can be written as follows (heating is symbolized by  $\Delta$ ):



The elimination does not take place always from the 1, 2 positions, and depending on which atoms are involved in the elimination, these reactions are classified as  $\alpha$ -eliminations,  $\beta$ -eliminations, 1,3-eliminations, etc. Based on their mechanism, these eliminations have either an  $E_i$  or a radicalic mechanism, and only in unusual cases an  $E_1$  or  $E_2$  mechanism. In  $E_2$  eliminations, a proton is pulled by a (Lewis) base and the  $\text{X}^-$  group departs simultaneously from the molecule. An  $E_2$  reaction occurs as follows:



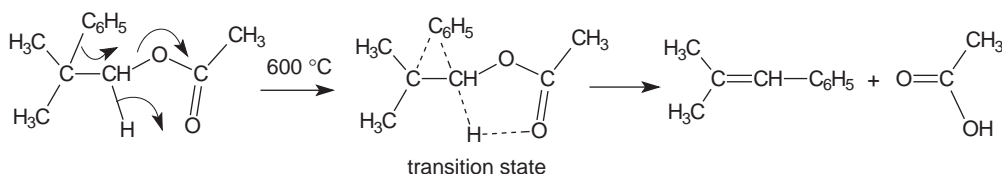
The reaction is bimolecular or  $E_2$ . In the  $E_1$  mechanism, the reagent loses an  $\text{X}^-$  group, typically to a solvent, to form a carbocation, and the rate determining process depends on only one species (therefore indicated as  $E_1$ ). The carbocation formation is followed by the rapid loss of a  $\beta$ -proton to a Lewis base. These mechanisms are not common in the case of pyrolysis in gas phase. However, when pyrolysis takes place in condensed phase, the  $E_2$  and  $E_1$  mechanisms are not excluded.

The  $E_i$  mechanism, which is very common in pyrolysis, involves a cyclic transition state, which may be four-, five-, or six-membered states [2]. No discrete intermediate is known in this mechanism (concerted mechanism). The radicalic mechanism involves more steps, the first being the formation of free radicals by bond cleavage. Also, the reactions with a radicalic mechanism are influenced by free radical inhibitors, while the reactions with  $E_i$  mechanism are not. The reactions with  $E_i$  mechanism are almost exclusively *syn* eliminations. The nature of the leaving group in the elimination reactions with  $E_i$  mechanism is very important.

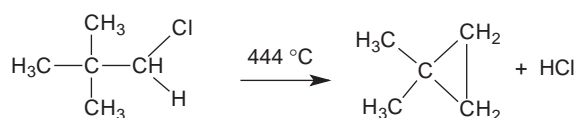


**$\alpha$ -Eliminations**

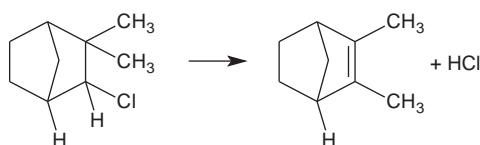
$\alpha$ -Eliminations involve two leaving groups connected to the same carbon (an  $\alpha$ -carbon is the carbon that attaches a functional group). They are encountered in some pyrolytic reactions where the more common  $\beta$ -elimination is not possible. One such case is the elimination of acetic acid from esters with alcohols containing a quaternary  $\beta$ -carbon, as shown in the following example [3]:



Similarly,  $\alpha$ -eliminations take place from an alkyl halide containing a quaternary  $\beta$ -carbon [4]:



An  $\alpha$ -elimination associated with a  $\text{CH}_3$  group migration takes place in a HCl elimination from 3-chlorocamphane as shown below:



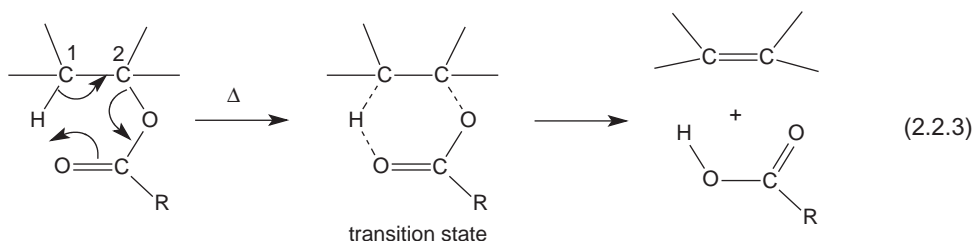
The unexpected  $\alpha$ -elimination of HCl is caused by the fact that the formation of a double bond at the bridgehead of the bicyclic compound is forbidden by the rule that a double bond cannot be placed at the bridgehead of a bridged ring system (Bredt's rule [5]).

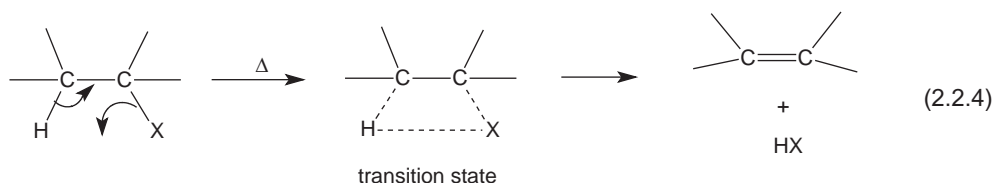
Silanes were also shown to pyrolyze involving  $\alpha$ -eliminations [6]. Some of the previously described reactions take place in parallel with other reactions, such that the product generated by  $\alpha$ -elimination is not the only component in pyrolysate.

 **$\beta$ -Eliminations**

Among pyrolytic eliminations,  $\beta$ -eliminations, with two groups lost from adjacent atoms, are probably the most common. These reactions take place typically by an  $E_i$  mechanism. Since pyrolytic elimination takes place with no other reagent present and often requires gas phase, the typical  $E_2$  mechanism where a proton is pulled by a base is not common.

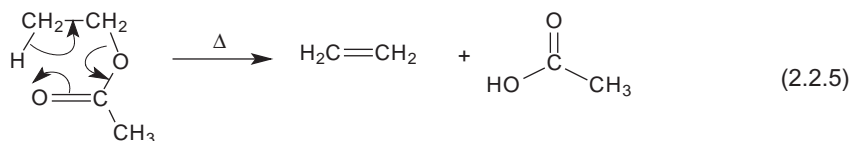
Two  $\beta$ -eliminations involving an  $E_i$  mechanism with different sizes of cyclic transition state are shown below [7]:



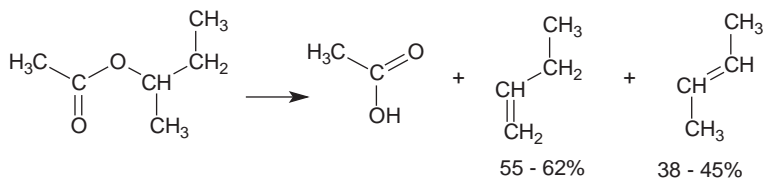


The two groups (one being the H in the above examples) leave at about the same time and bond to each other. However, the perfect equivalence of the cleavage of the two bonds is not always achieved. For example, in the case with X a halogen in reaction 2.2.4, the C–X bond is split to a greater extent than the C–H bond, creating a carbocation character in the transition state. This process is in agreement with Woodward–Hoffmann rules, which imply that a completely nonpolar four-member cyclic transition state is not allowed for these molecules. The carbocation character of the transition state is also in agreement with the measurements of the reaction rates for the elimination that are in the order  $I > Br > Cl > F$ . The ester elimination reactions are closer to a pure  $E_i$  mechanism, with the two groups leaving at about the same time.

Many examples of  $\beta$ -eliminations occur in practice, the most typical being the elimination of an acid from an ester containing a hydrogen on the  $\beta$ -carbon of the alkoxy group [8]. One such example is the pyrolysis of ethyl acetate, which forms upon heating ethylene and acetic acid:

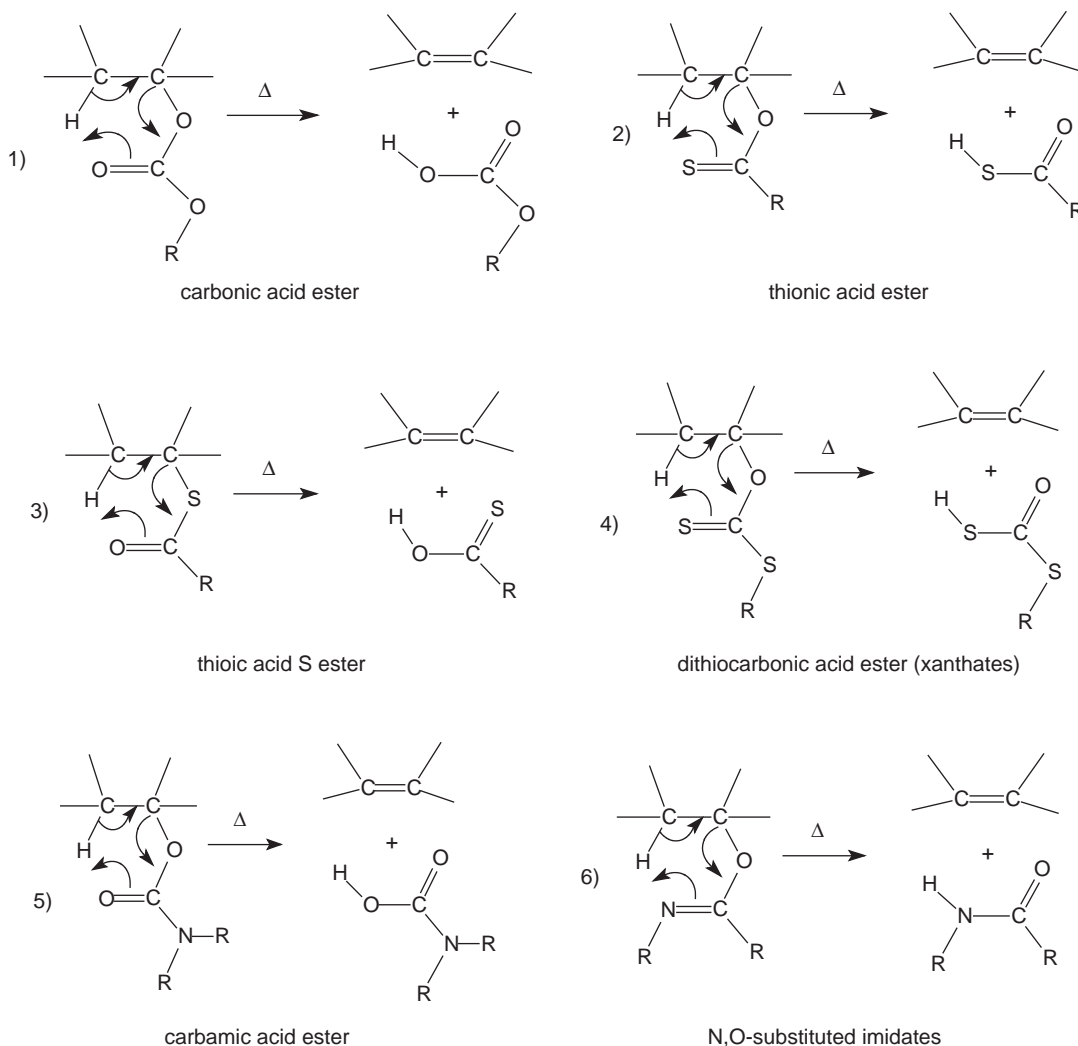


The  $E_i$  mechanism is characterized by first order kinetics, the lack of free radicals (free radical inhibitors do not slow down the reaction), and by the fact that the elimination takes place in a *syn* position. During pyrolytic reactions of  $E_i$  type, if a double bond is present, the formation of a conjugate system is preferred if sterically possible. Otherwise, the orientation in the pyrolytic elimination is statistical and is determined by the number of  $\beta$ -hydrogens. The newly formed double bond goes more toward the least substituted carbon (Hofmann's rule), as shown in the following example:



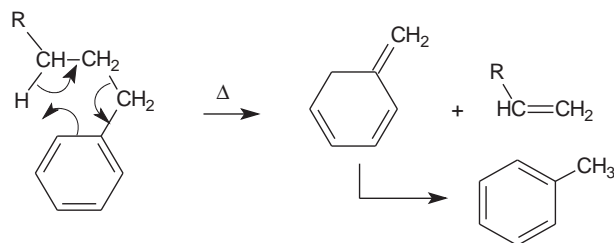
In the bridged systems, the double bond is formed away from the bridgehead. Also, for the  $E_i$  mechanism in a planar molecule, a *cis*  $\beta$ -hydrogen is required. In cyclic systems, with a *cis* hydrogen on only one side of the molecule, the double bond will be formed from this hydrogen [2]. However, when there is a six-membered transition state, this does not necessarily mean that the leaving groups must be *cis* to each other, since six-membered states are not completely coplanar. Since the axial (*a*) groups alternate in direction, two axial groups in  $\beta$ -position are always *trans*. Therefore, if the leaving group is axial (*a*), then the hydrogen must be equatorial (*e*) to the leaving group, since the transition state cannot be realized when the groups are both axial (and *trans* to each other). When the leaving group is equatorial, it can form a transition state with a  $\beta$ -hydrogen that is either axial (*cis*) or equatorial (*trans*). These types of reactions may be seen during the elimination of HCl in pyrolysis of lindane (eeeeee 1,2,3,4,5,6-hexachlorocyclohexane) (see Section 8.1).

There are some other  $\beta$ -eliminations from compounds similar to those occurring in esters, and several cases are as follows:

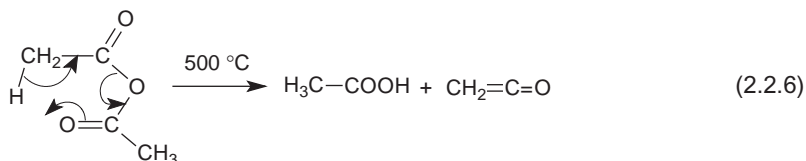


Even if many  $\beta$ -eliminations take place with high yields, it is typical for pyrolysis to have simultaneous incidence of multiple reaction paths, and, depending on the specific compound pyrolyzed, the yield for the  $\beta$ -elimination can vary considerably [9]. Also, some rearrangements may continue after the initial step of the elimination.

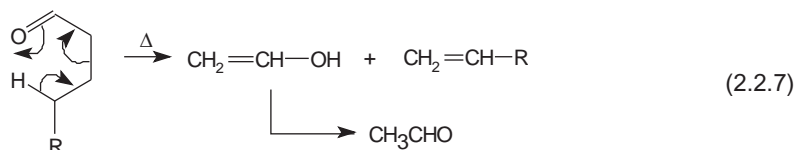
$\beta$ -Eliminations may take place without involving any heteroatoms, as shown in the thermal decomposition of certain alkyl-aromatic hydrocarbons:



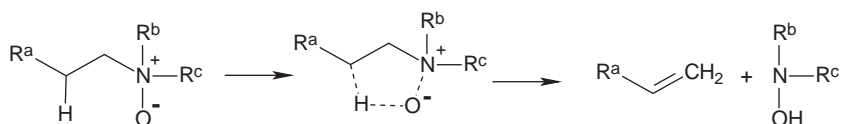
Other  $\beta$ -elimination reactions include the formation of ketenes from the pyrolysis of esters, anhydrides, and acyl chlorides as shown for acetic anhydride:



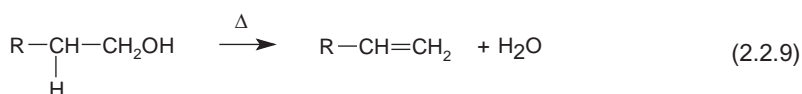
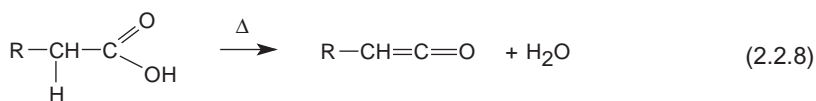
Besides esters or ester-like compounds,  $\beta$ -eliminations are also common for other compounds, including certain ketones where the thermal decomposition takes place as follows:



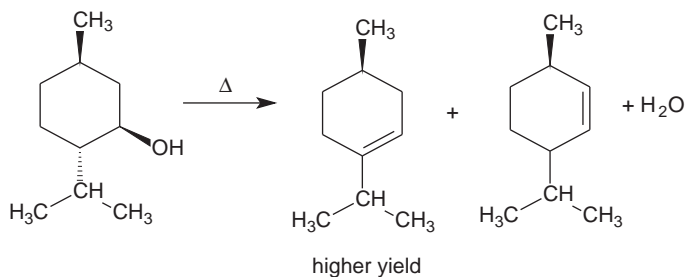
Another example of  $\beta$ -elimination is that suffered by amine oxides (Cope elimination), generating an alkene and a hydroxylamine as shown below:



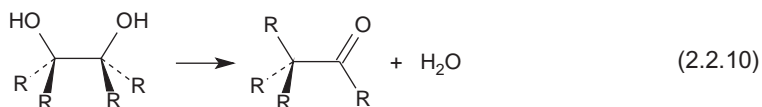
Other  $\beta$ -eliminations involve the elimination of water from some carboxylic acids and from alcohols. These types of reactions are shown below:



For example, water elimination takes place during the pyrolysis of menthol (natural menthol is (1R,2S,5R)-(-)-menthol) to form 3-menthene (4-methyl-1-(1-methylethyl)-cyclohexene) and some 2-menthene (3-methyl-6-(1-methylethyl)-cyclohexene).

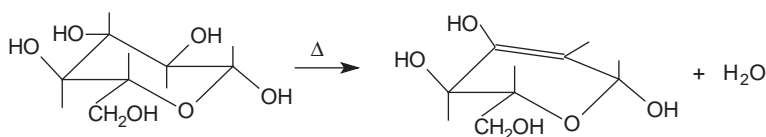


A well-known  $\beta$ -elimination of  $\text{H}_2\text{O}$  takes place from substituted 1,2-diols. The reaction was first identified for 2,3-dimethylbutane-2,3-diol (pinacol) and for this reason, it is named pinacol rearrangement. The reaction is shown below:



The reaction typically takes place in acidic conditions, when it has a nucleophilic mechanism, but it is also noticed during pyrolysis.

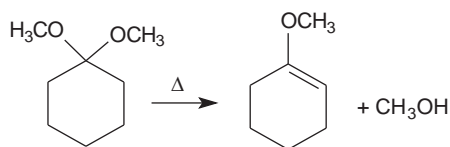
For larger molecules, it is not always possible to assign an  $\text{E}_i$  mechanism to the elimination. An example is the elimination of water during the pyrolysis of glucose:



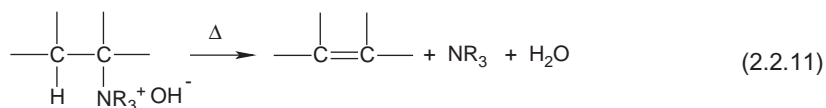
This reaction may have either an  $\text{E}_i$  mechanism or an  $\text{E}_2$  mechanism because it takes place in condensed phase. The impurities in the pyrolyzed material may act as a proton acceptor (see reaction 2.2.2). The presence of traces of a strong base ( $\text{NaOH}$ ) will favor the  $\text{E}_2$  mechanism, with the base pulling off the protons during dehydration.

Besides the  $\text{E}_i$  mechanism, in some cases, an  $\text{E}_1$  elimination mechanism can occur, resulting in a more stable olefin. Instead of Hofmann's rule, Zaitsev's rule is followed (the double bond goes mainly toward the most highly substituted carbon). In some reactions, the direction of elimination is determined by the need to minimize steric interactions, sometimes even when the steric hindrance appears only during the transition state.

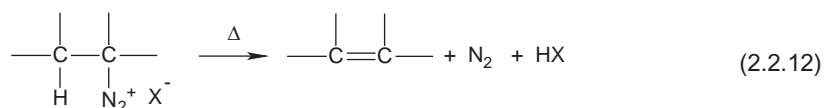
Water is not the only molecule eliminated in a  $\beta$ -elimination. Acetals and ketals eliminate an alcohol molecule by pyrolysis, as shown below for cyclohexanone dimethylketal:



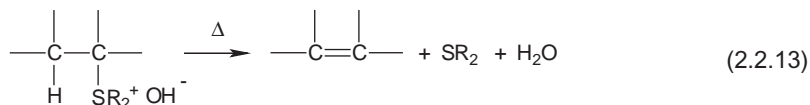
Similar to the elimination of  $\text{H}_2\text{O}$  from alcohol, the elimination of  $\text{H}_2\text{S}$  takes place from thiols. Also, quaternary ammonium hydroxides eliminate trialkylamines and water:



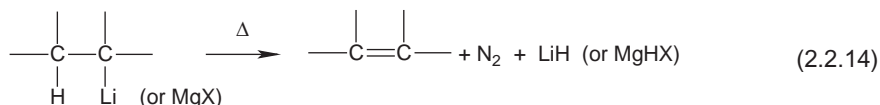
Diazonium salts form olefins by a similar reaction:



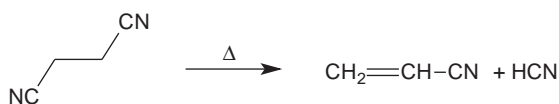
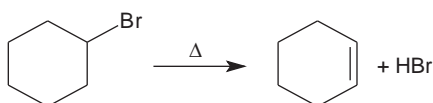
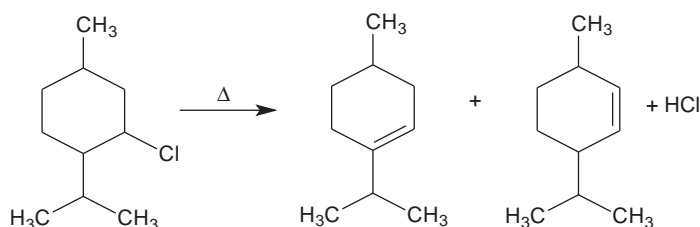
Sulfonium compounds undergo a similar reaction:



Even organometallic compounds decompose at elevated temperatures involving a  $\beta$ -elimination, as shown in the following example:



Hydrochloric acid, other hydrohalogenated acids, and hydrogen cyanide can also be produced in  $\beta$ -eliminations. Some examples are given below:

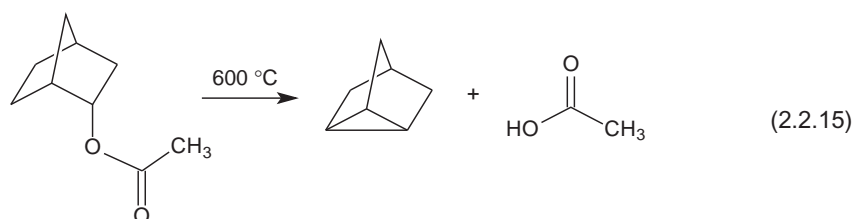


The elimination of HX may take place not only by a concerted mechanism but also by a radicalic one.

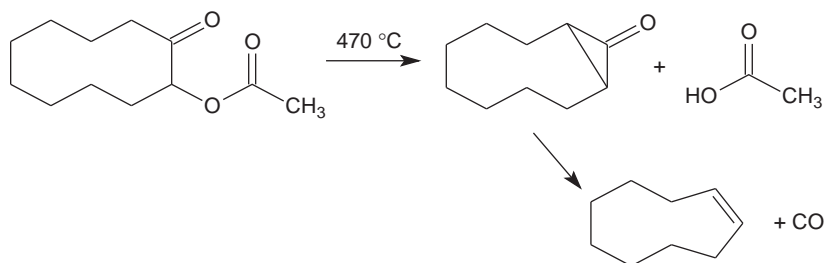
The double (or triple) bond formation in eliminations does not take place exclusively between carbon atoms. It may lead to the formation of double bonds between carbon and nitrogen or carbon and oxygen.

### 1,3- and 1,n-eliminations

In addition to  $\beta$ -eliminations, 1,3- and 1,*n*-eliminations may take place during pyrolysis. One example of a 1,3-elimination is shown below for bicyclo[2.2.1]heptan-2-yl acetate to form tricyclo[2.2.1.0<sup>2,6</sup>]heptane [10]:

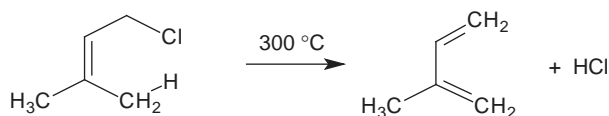


A small amount of 2-norbornene is also formed in this reaction. The formation of certain stable cycles takes place in this manner, but some of the 1,3-eliminations may proceed followed by rearrangements or further reactions and may not be viewed initially as 1,3-eliminations. One such example is given below for 2-hydroxycyclodecan-1-one acetate, which generates cyclonon-1-ene [11]:

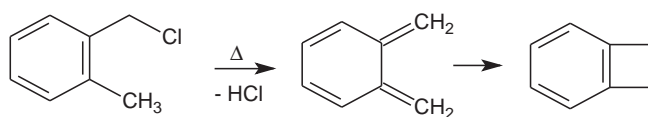


In addition to a  $\gamma$ -elimination, other reactions, including  $\beta$ -eliminations, take place during the pyrolysis of 2-oxocyclodecyl acetate.

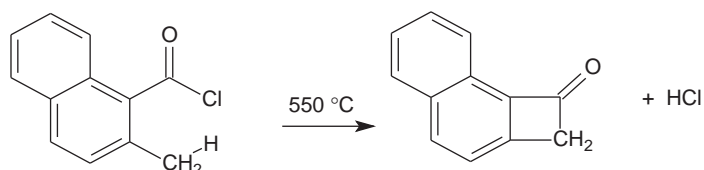
A number of 1,4-eliminations are reported in the literature [12,13]. A typical example is the elimination of HCl from 1-chloro-3-methyl-2-butene:



Similarly, *o*-methylbenzyl chloride generates 1,2-dihydrocyclobuta[1,2-*a*]benzene following a rearrangement of the 1,2-dimethylenecyclohexa-3,5-diene formed as an intermediary [14]:

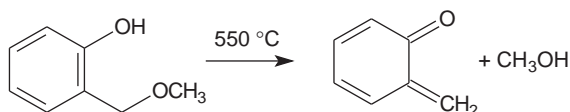


Acyl chlorides react similarly, as shown in the reaction of 2-methylnaphthalene carboxylic acid chloride, which generates 2-hydrocyclobuta[2,1-*a*]naphthalen-1-one [15]:



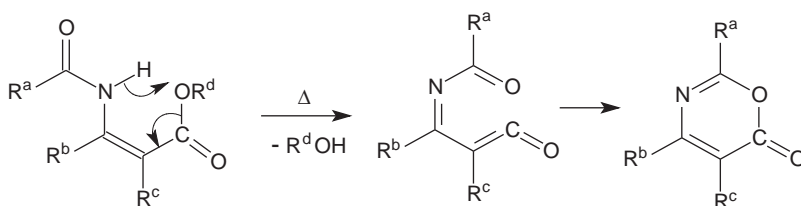
Similar to the elimination of HCl, an alcohol can be eliminated, for example, from substituted phenols, as shown in the following reaction for 2-(methoxymethyl)phenol, which generates

2-methylenecyclohexa-3,5-dien-1-one [16]:

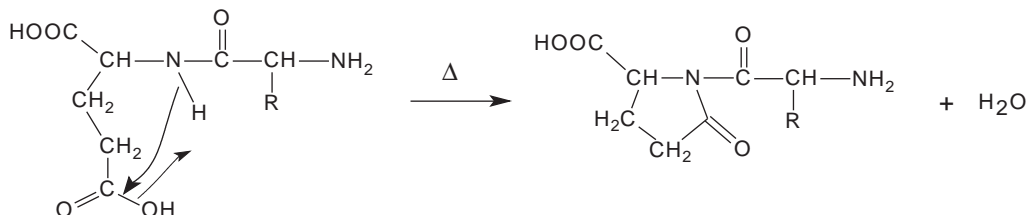


The pyrolysis product was isolated at  $-196^{\circ}\text{C}$  and formed a trimer at room temperature. Other similar reactions followed by rearrangements are reported in the literature [17]. The mechanism of 1,4-eliminations is not always of E<sub>i</sub> type. The elimination reaction may take place with a carbocation as a leaving group, when the elimination is known as a fragmentation reaction.

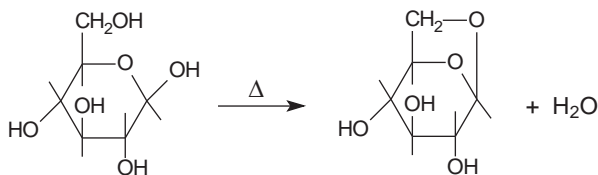
An example of a 1,3-elimination of an alcohol is the formation of substituted 1,3-oxazin-6-ones from 3-acylaminoacrylic acid esters following the reactions shown below [18]:



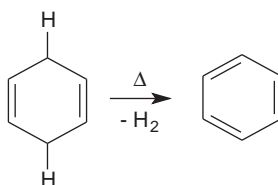
A similar 1, $n$ -elimination occurs during the pyrolysis of certain peptides. A glutamic acid unit, for example, can eliminate water to form a pyrrolidinone cycle by the following reaction:



Water elimination may also take place in a 1, $n$ -elimination, for example, from glucose, with formation of 1,6-anhydro- $\beta$ -D-glucose (levoglucosan):



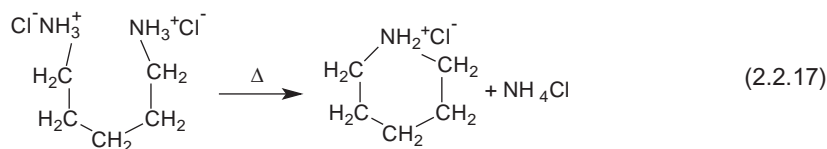
1,4-Hydrogen elimination, although not a very common reaction, is encountered, for example, during pyrolysis of 1,4-cyclohexadiene:



(2.2.16)



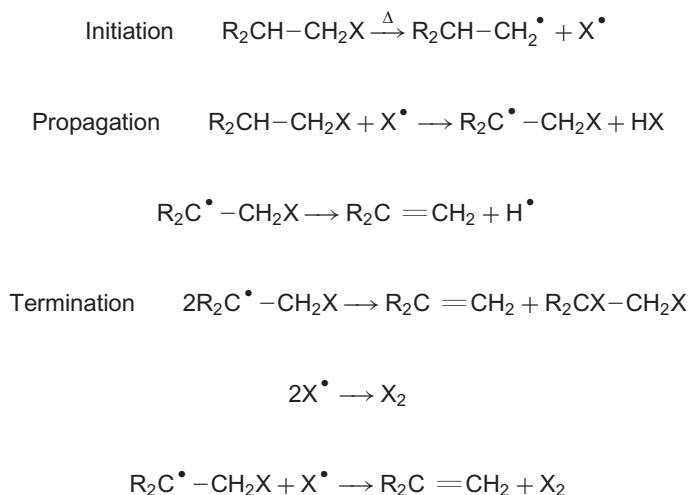
An interesting elimination takes place during the pyrolysis of 1,2-, 1,4-, and 1,5-diamine hydrochlorides, which on thermal decomposition eliminate  $\text{NH}_4\text{Cl}$  and form cyclic amines (in hydrochloride form). Putrescine forms pyrrolidine, while cadaverine forms piperidine. The reaction for cadaverine is shown below:



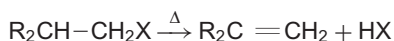
For ethylenediamine hydrochloride, the elimination is intermolecular and leads to piperazine. The mechanism of these eliminations is in fact that of a nucleophilic substitution (see Section 13.3).

### Eliminations involving free radicals

A common type of mechanism found to operate in pyrolytic eliminations involves free radicals. First, an initiation occurs by pyrolytic cleavage, followed by propagation and termination with the result of molecular fragments formation. A schematic example of free radical elimination is presented as follows:



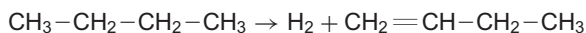
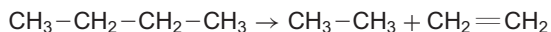
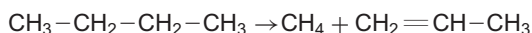
The main result of the reaction (excluding small amounts of other compounds resulting from termination reactions) can be written as follows:



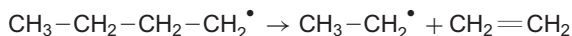
Free radical eliminations are frequent at temperatures between 600 °C and 900 °C. The initiation reaction typically takes place with a higher probability at the bonds with a lower energy (see Section 3.1). However, at higher temperatures, even bonds with higher energy are cleaved. The stability of the free radicals that are formed in these reactions also plays an important role in the initiation mechanism.

Propagation reactions can have various paths. This explains in part the complexity of pyrolysates even from simple molecules such as aliphatic hydrocarbons that generate other aliphatic compounds, as well as unsaturated and aromatic hydrocarbons (and also char [19]). Frequently, pyrolysis takes place in several stages, with further decomposition of the compounds generated in the first stage. For example, butane thermal decomposition generates different compounds depending on temperature,

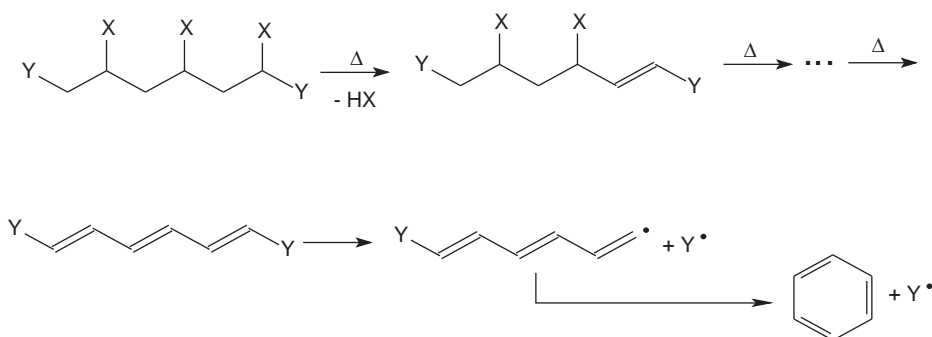
gas pressure, and pyrolysis time. A few reactions that occur in the first stage of butane pyrolysis are shown below:



In general, propagation reactions with free radical formation, besides intermolecular reactions, may include intramolecular reactions such as  $\beta$ -scissions and isomerizations (back biting). The generated compounds do not have equal distribution. Some reactions during pyrolysis have a higher probability than others, depending on the molecular structure of the initial compound and of the products. For example, after the formation of a free radical, when possible, the  $\beta$ -scissions to the atom bearing the unpaired electron are favored compared to other scissions. For a free radical like 1-butyl, the main scission process of the radical is the following:



In some pyrolytic processes, a radicalic mechanism may be involved only in secondary stages of the process. When other reactions occur at higher rates than the formation of free radicals, intermediate products are formed, and these may further pyrolyze involving free radicals. An example is the formation of an aromatic compound involving radicals after an elimination that does not involve radicals. This type of process is illustrated in the following reactions:

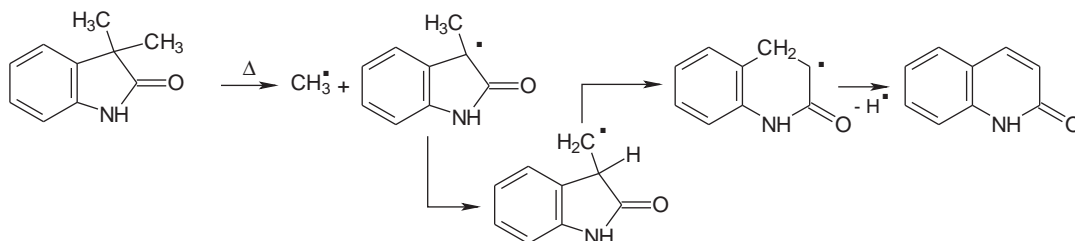


where X and Y can be either H or another group. The elimination of HX or of YY smaller molecules depends on the nature of X and Y substituents.

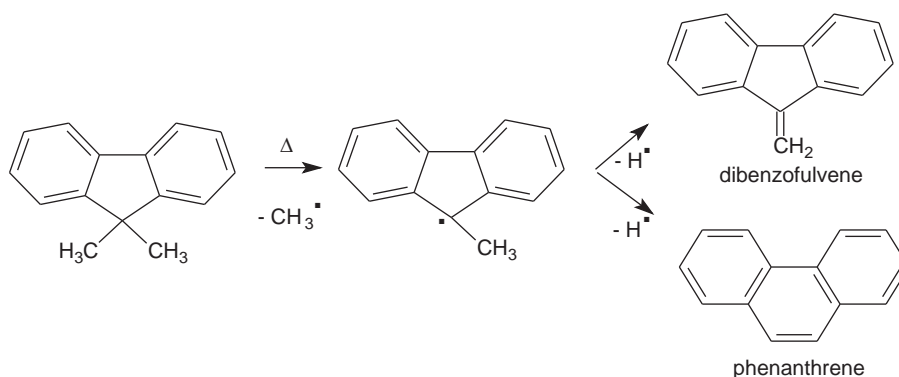
Termination reactions also contribute to the final composition of pyrolysates and therefore to their complexity. Depending on the kinetics parameters of the reactions (see Section 3.2) and on pyrolysis conditions (temperature, pressure), the terminations may be more or less important. For example, at higher pressures, when the concentration of free radicals increases, the interaction between these free radicals undergoing termination reactions may be predominant compared to the propagation reactions. This may lead to a different composition of the pyrolysate for gaseous compounds at higher pressure compared to that obtained at the same temperature and lower pressure. For solids, in flash pyrolysis, the pressure has a lesser role.

The elimination reactions taking place with a free radical mechanism can be followed by rearrangements also involving free radicals. One such example is shown below for

3,3-dimethyl-2,3-dihydroindole-2-one, which forms 2(1H)-quinolinone [20]:

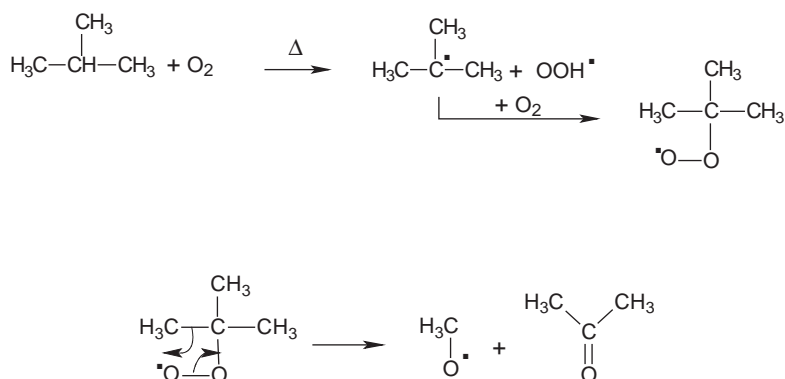


In a similar chain of reactions, 9,9-dimethylfluorene generates phenanthrene and dibenzofulvene (9-methylenefluorene) [21]:



Eliminations involving free radicals are important in burning reactions. Hydrocarbons react with oxygen, forming  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ , but a number of other oxygenated compounds are also obtained when burning is performed in controlled conditions and in a limited quantity of oxygen. A mixture of propane and butane, for example, in limited oxygen generates acetaldehyde, methyl formate, formaldehyde dimethyl acetal, propionaldehyde, acrolein, acetone, acetaldehyde dimethyl acetal, tetrahydrofuran, methanol, ethanol, 1-propanol, 2-propanol, ethyl methyl ketone, formaldehyde, formic acid, 1-butanol, 1,2-ethandiol, and 1,2-propandiol.

Formation of acetone in the incomplete combustion of isobutane is illustrated below as an example:



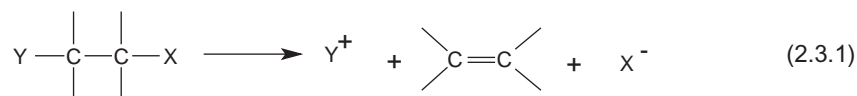
In the presence of oxygen, acetone continues the oxidation reaction. Similar reactions can explain the formation of other compounds during hydrocarbon burning.

### 2.3. FRAGMENTATION AND EXTRUSION REACTIONS

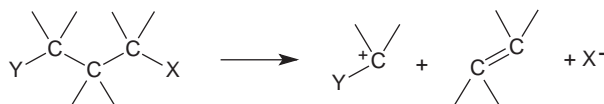
#### Fragmentations

The simple meaning of fragmentation is the breaking of a molecule A–B into two parts A and B (with potentially rearranged bonds in the fragments A and B). However, a single two-electron bond cleavage usually generates either ions or radicals (in some special cases, the cleavage generates carbenes or nitrenes). Therefore, the formation of neutral new molecules A and B (with complete number of electrons) is not possible without the transfer of one part of molecule A to molecule B, or vice versa. True fragmentations are common when the molecules are subject to an electron bombardment as used in mass spectrometry.

A special type of fragmentation known as Grob fragmentation is a specific type of elimination reaction where one carbocation is the leaving group. This type of reaction commonly takes place in substances of the form Y–C–C–X, where X could be OH<sub>2</sub><sup>+</sup>, OTs, NR<sub>3</sub><sup>+</sup>, etc. (Ts is *p*-toluenesulfonate or tosylate). The fragmentation can be written schematically as follows:

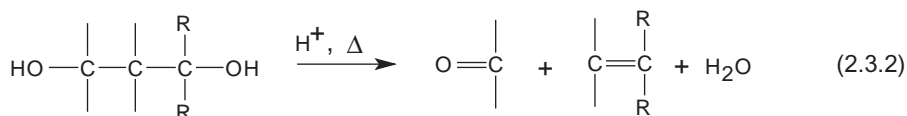


When the electrofuge and the nucleofuge are situated in positions 1 and 3 on an aliphatic chain, this type of fragmentation is known as Grob fragmentation. The reaction product is an electrofugal fragment (carbonium ion, acylium ion), an unsaturated fragment (alkene, alkyne, imine), and a nucleofugal fragment (leaving group such as tosyl or hydroxyl).

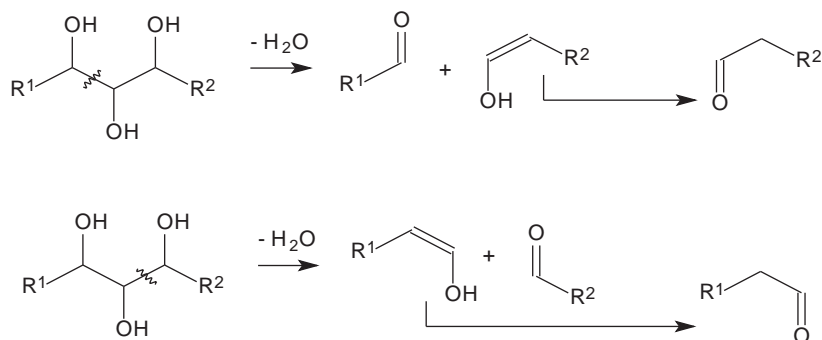


The reaction mechanism can be concerted (E<sub>i</sub>), taking place in two steps, with the formation of a carbocationic intermediate when the nucleofuge leaves first, or with the formation of an anionic intermediate when the electrofuge leaves first.

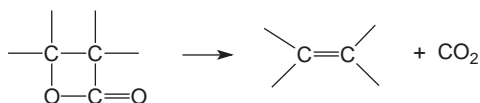
An example of Grob fragmentation reaction is the following dehydration of 1,3-diols:



This type of Grob fragmentation is also typical for carbohydrates, even when they are in cyclic form, since 1,3-diol groups are present in these molecules. Depending on the substituents on the carbons bound to the OH groups, Grob fragmentation may take place in two different manners, as indicated below for a 1,2,3-triol:

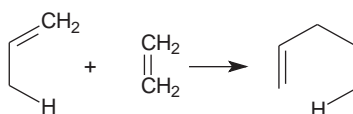


The decomposition of  $\beta$ -lactones can also be included in this type of fragmentation and can be applied to the decomposition of ketene dimers as shown in the reaction below:

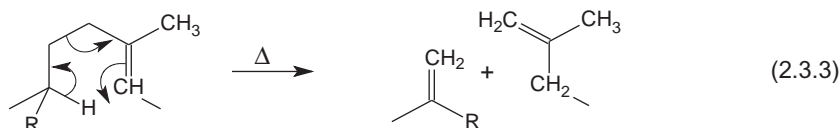


### Retro-ene reactions

Another known fragmentation is the retro-ene reaction. The hydro-allyl addition reaction exemplified for the formation of pentene from ethene and propene is shown below:

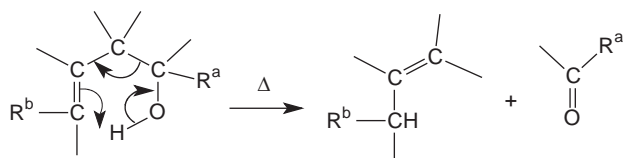


The reverse hydro-allyl addition (retro-ene reaction) occurring during pyrolysis takes place as follows:

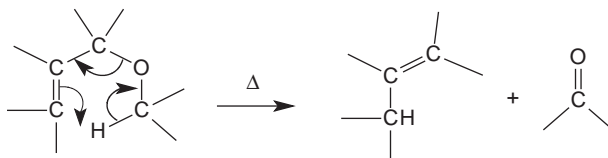


Some retro-ene reactions may take place involving free radicals. For example, thermal decomposition of 1-pentene may take place with the formation of ethyl and allyl radicals, which further generate ethene and propene.

Carbon atoms are not the only ones able to participate in retro-ene reactions.  $\beta$ -Hydroxy olefins, for example, undergo a retro-ene fragmentation as follows:

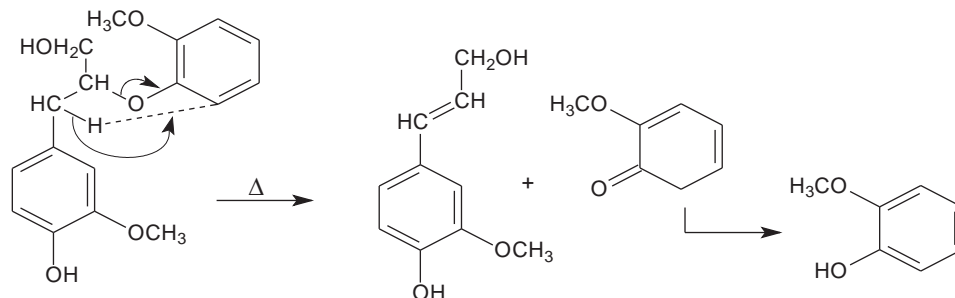


This reaction occurs with good yields when the radicals  $\text{R}^a$  and  $\text{R}^b$  are long alkyl chains. Also, allylic ethers and allylic esters undergo a similar elimination with the formation of aldehydes or ketones:



A reaction similar to that of allylic ethers is the formation of coniferyl alcohol and *o*-methoxyphenol during the pyrolysis of 4-[3-hydroxy-2-(2-methoxyphenoxy)propyl]-2-methoxyphenol (a lignin

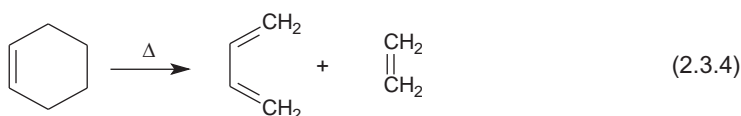
degradation product):



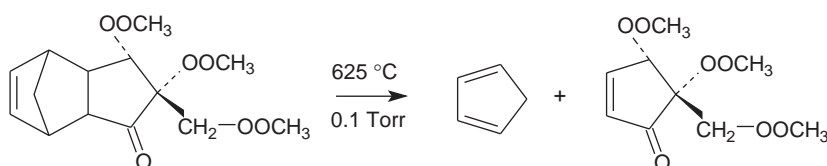
Some other examples of retro-ene reactions involve heteroatoms. For example, sulfur may replace the oxygen atom in allylic ethers, and some thiones can be obtained from the pyrolysis of allyl sulfides [22].

### Retro-Diels–Alder condensations

The cycloaddition reaction of a conjugated diene with a compound containing a multiple bond is known as Diels–Alder reaction. The retro-Diels–Alder reaction takes place as the reverse of the Diels–Alder reaction, and is exemplified below for the simple case of cyclohexene:

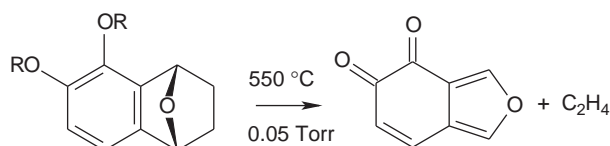


This reaction is quite common in pyrolysis and also has been used for specific synthetic purposes. For example, pentenomycin I, an antibiotic produced by *Streptomyces eurythermus*, has been synthesized using a pyrolytic retro-Diels–Alder reaction [23]:



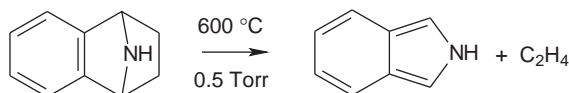
The antibiotic was obtained by hydrolysis of the acetylated compound. It is interesting that the steric configuration of the initial substance was not modified during pyrolysis.

Ethylene can be eliminated in a retro-Diels–Alder reaction of the type [22]:



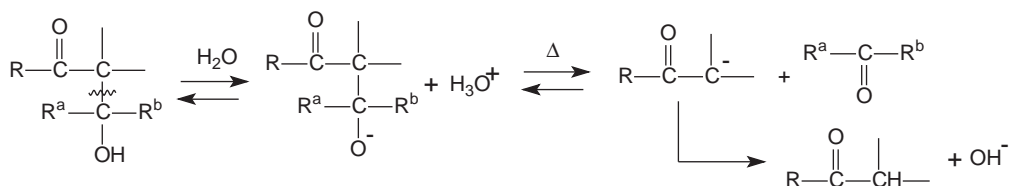
Besides the elimination of cyclopentadiene, the elimination of fulvene and furan may also take place during pyrolysis from some of their Diels–Alder adducts [17]. The same type of reaction has been used

for the preparation of isoindole as shown below:

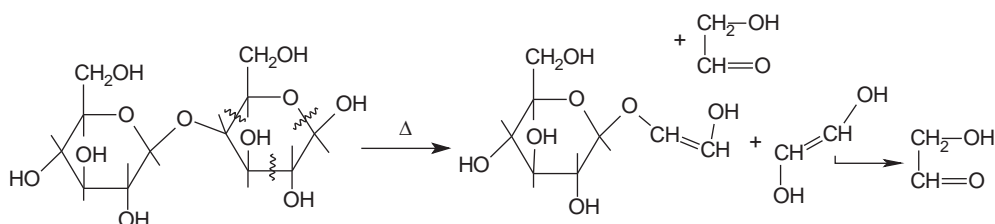


### ***Retro-aldol condensations***

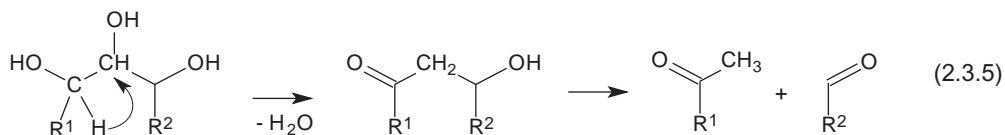
Retro-aldol condensations are known to take place during pyrolysis, and they may be viewed as fragmentation reactions. The mechanism of these reactions can be written as follows:



This type of reaction is not likely to take place in gas phase but can occur in solid phase during pyrolysis. The mechanism involves the presence of a water molecule, which can be present in the sample in many cases. Pyrolysis of cellobiose with formation of hydroxyacetaldehyde may take place following such a mechanism:



The retro-aldol condensation may follow in carbohydrates a pinacol type rearrangement with the shift of a hydrogen atom, as shown in the sequence of reactions below:



This type of sequence of reactions can be encountered during carbohydrates and polyol pyrolysis.

## Extrusions

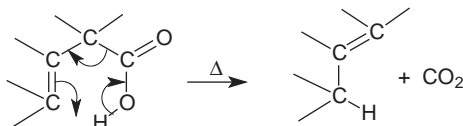
Contrary to the breaking of one single covalent bond, which generates ions or radicals, when two bonds break simultaneously, new neutral molecules (with even number of electrons) can be formed. This type

of elimination is indicated as extrusion and can be written as follows:

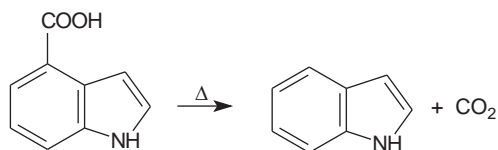


where A is typically a small molecule such as CO, CO<sub>2</sub>, COS, N<sub>2</sub>, or SO<sub>2</sub>.

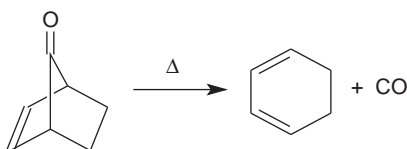
The extrusion reactions may take place from acyclic structures, such as in the case of decarboxylation of  $\beta$ -unsaturated acids:



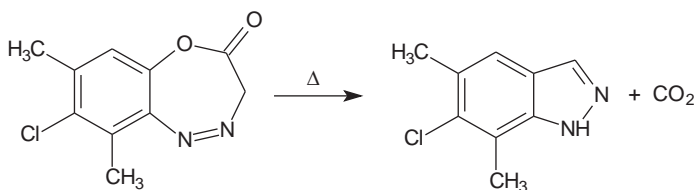
Decarboxylation of other carboxylic acids can be included in this type of reaction, as shown below for indole-4-carboxylic acid:



Extrusion reactions are more common for cyclic structures. The elimination of CO from some cyclic ketones is a typical case, as shown for norborn-2-en-7-one (bicyclo[2.2.1]hept-2-en-7-one):



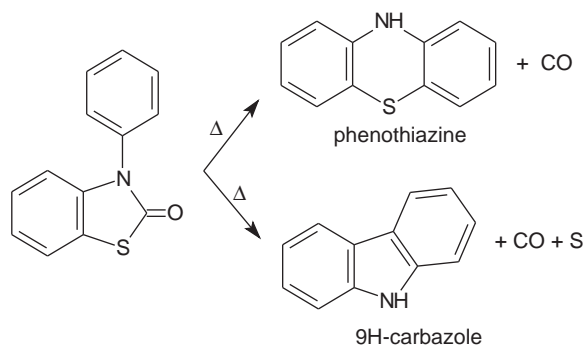
Elimination of CO<sub>2</sub> is possible by extrusion reactions from certain lactones, as shown in the following example with the formation of a 1H-indazole derivative [2]:



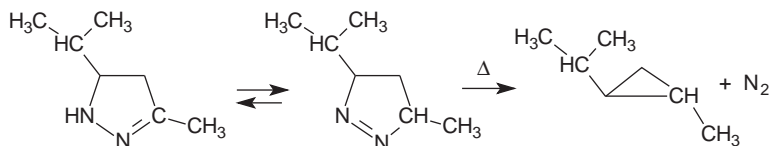
Many other cyclic structures, including heterocyclic ones, undergo extrusion reactions during pyrolysis. For example, pyrolysis of 1-phenylbenzothiazolin-2-one takes place with the formation of



phenothiazine and of 9H-carbazole as follows [24]:

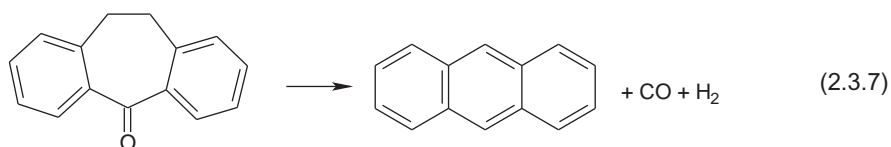


Pyrolysis of pyrazolines with the extrusion of  $N_2$  leads to the formation of cyclopropane derivatives, as shown below for 4,5-dihydro-3-methyl-5-(1-methylethyl)-1H-pyrazole:



During pyrolysis, numerous other fragmentation reactions may occur, although the mechanism is not always of the  $E_i$ ,  $E_1$ , or  $E_2$  type (see eliminations involving radicals).

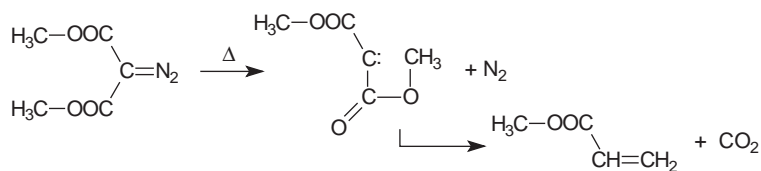
A reaction that can be included in extrusion category is the formation of anthracene from 10,11-dihydro-5H-dibenzo[*a,d*]cyclohepten-5-one (dibenzosuberone) [17], as shown below:



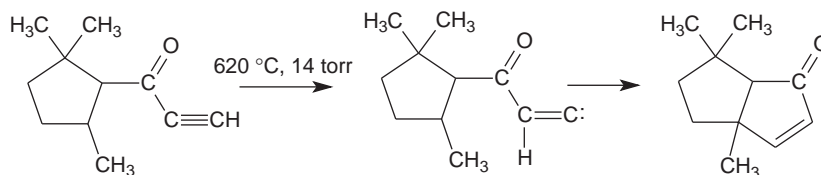
Reaction 2.3.7 is encountered for other dibenzoannulenes and shows regiospecificity (see Section 2.4).

### Formation of carbenes and nitrenes

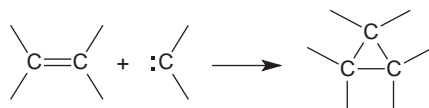
Carbenes are reactive compounds with the carbon atom having a six-electron configuration. Similarly, in nitrenes, a nitrogen atom has only six electrons. Carbenes are formed, for example, during the pyrolysis of  $\alpha$ -diazocarboxyl compounds, as shown below for dimethyldiazomalonate [22]:



Carbenes are also formed in some pyrolytic reactions of substituted acetylenes, leading to further rearrangements and new cycles formation, as shown below for ethynyl-2,2,5-trimethyl-1-cyclopentyl ketone [25]:

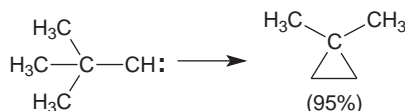


The high reactivity of carbenes can even lead to the formation of cycles with three or four atoms. Addition of carbenes to a double bond or triple bond leads to cyclopropane derivatives, as shown in the reaction below:



Depending on the substituents, the resulting cyclopropane can be stable, or it can be unstable and undergo further isomerization.

The high reactivity of carbenes can manifest also by intramolecular insertion reactions. For example, the carbene from butane (butylidene) reacts upon heating as follows:



It is not uncommon that the pyrolysis products contain cyclopropane derivatives. Intramolecular insertion reactions are also possible.

Nitrenes can be generated, for example, from pyrolysis of azides with the elimination of  $N_2$ . These substances are not stable and generate more stable compounds through different rearrangements. Both carbenes and nitrenes may react with other compounds through a hydrogen abstraction and generate a pair of free radicals.

### Fragmentation in pyrolytic reactions compared to ion fragmentation in mass spectroscopy

Various attempts to find similarities between the fragmentation (with the simple meaning of the concept) taking place in pyrolytic reactions and fragmentation of molecules seen in their mass spectrum [26–29] are reported in the literature. In mass spectrometry, molecules are fragmented following an ionization step (positive electron ionization +EI). This ionization is commonly done using an electron bombardment with electrons having energy of 70 eV and at a very low pressure (in vacuum  $10^{-2}$  to  $10^{-3}$  Pa). During pyrolysis, there are no ions formed because the energies involved in the pyrolytic process are much lower than the required level for ion formation (ionization potentials of many molecules are around 10 eV). Also, pyrolysis is done for many molecules in condensed phase and can be performed at different temperatures. These essential differences make the two processes different. However, the fragmentation seen in a mass spectrum of a compound and the fragments generated by its pyrolysis frequently display obvious similarities. In general, the complexity of the pyrolysate and the complexity of the mass spectrum are both either high or low. Also, the nature of molecular fragments generated in pyrolysis shows similarities with that of the ions generated in a mass spectrometer. As an

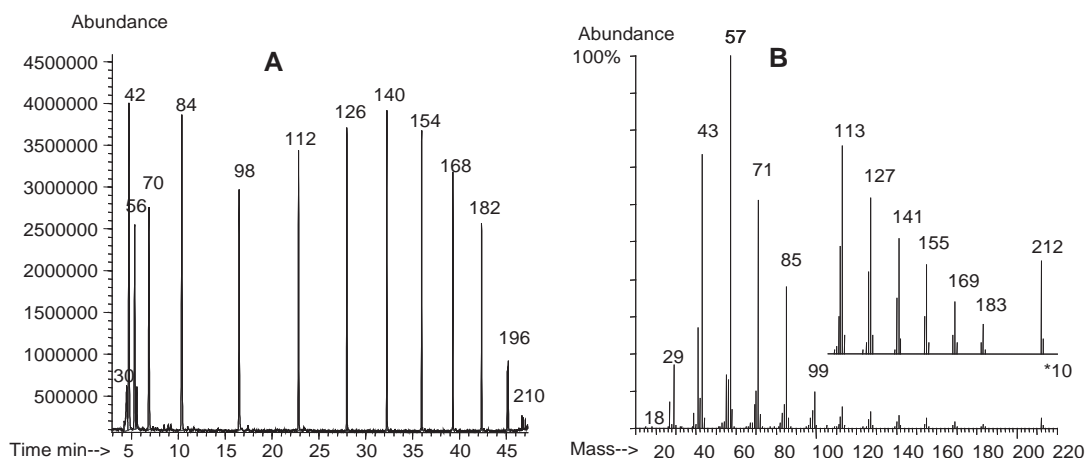


FIGURE 2.3.1. (A) Chromatogram of pentadecane pyrolysate with the molecular mass of each component indicated above the peak. (B) Mass spectrum of pentadecane showing the mass of each fragment ion. Note: In this book, the molecular weight (MW) of molecules and fragments is given for the most abundant natural isotope and rounded to integers.

example, a chromatogram of a pentadecane pyrolysate (see Section 7.1) and the +EI spectrum of pentadecane are shown in Figure 2.3.1A and 2.3.1B, respectively.

In Figure 2.3.1A, the chromatographic peaks eluting at different retention times (and labeled with their molecular mass instead of retention time) are components from the pyrolysate of pentadecane. The compounds are alkenes: ethene (MW = 30), propene (MW = 42), 1-butene (MW = 56), 1-pentene (MW = 70), 1-hexene (MW = 84), ... up to 1-pentadecene (MW = 210). In Figure 2.3.1B, the spectrum of pentadecane is given, and the fragment ions correspond to the positive ions:  $\text{C}_2\text{H}_5^+$  ( $m/z = 29$ ),  $\text{C}_3\text{H}_7^+$  ( $m/z = 43$ ),  $\text{C}_4\text{H}_9^+$  ( $m/z = 57$ ),  $\text{C}_5\text{H}_{11}^+$  ( $m/z = 71$ ),  $\text{C}_6\text{H}_{13}^+$  ( $m/z = 85$ ), etc. There is an obvious similarity between the pyrolysis fragmentation and mass spectral fragmentation. The peak areas in Figure 2.3.1A depend on the amount of material in the pyrolysate. By normalizing these areas with the molecular weight of each compound, the similarity with the mass spectrum is even more evident. The analogy between the two processes shown for pentadecane is common for many compounds. This can be seen, for example, when free radicals are involved in pyrolysis, when rearrangements take place, and when retro-Diels–Alder reactions occur. Internal displacement reactions may also be similar in the two processes. The relationship between mass spectra and thermal fragmentation is complex, involving numerous factors. For example, the thermal process has in general a higher stereoselectivity, since it involves lower energies. Also, since aromaticity is possible in even-electron systems and not likely in the odd-electron fragments that are generated in mass spectrometry, pyrolytic processes have a higher tendency to form aromatic compounds compared to the formation of ions of aromatic species (e.g.,  $\text{C}_6\text{H}_5^+$ ) from nonaromatic compounds. In spite of differences, the mass spectrum of a compound provides hints regarding the complexity of its pyrolysate as well as of potential constituents of the pyrolysate.

## 2.4. REARRANGEMENT REACTIONS

### General aspects

Rearrangements are very common in pyrolytic reactions following eliminations (mainly when they involve a radicalic mechanism) and fragmentations. Some examples of such rearrangements were presented previously. However, some rearrangements take place without association with another reaction. Among these are, for example, migrations of a group from one atom to another (in the same molecule). Some examples of such migrations take place from one atom to an adjacent one (1,2-shift),

but migrations over higher distances are possible in pyrolysis. A typical 1,2-shift takes place as follows:

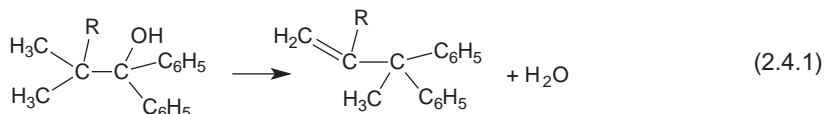


The migration group M may move with its electron pair, without its electron pair, or with only one electron. In the last case, a free radical rearrangement takes place. The free radical rearrangement involves as a first step the formation of free radicals, followed by the actual migration. During pyrolysis, the formation of free radicals is rather common, but they do not necessarily lead to 1,2-shifts. The 1,2-type shifts are more common in nucleophilic reactions and less common in pyrolysis. More complicated mechanisms of migration may involve diradical formation [2].

Among non-1,2 rearrangements that occur during pyrolysis, one important group is that of electrocyclic rearrangements, which take place with the migration of a bond in systems containing six  $\pi$  electrons. Also, the sigmatropic rearrangements are non-1,2-shifts. This type of rearrangement consists of a concerted migration of a  $\sigma$  bond adjacent to one or more  $\pi$  systems to a new position in the molecule, with a new reorganized  $\pi$  system.

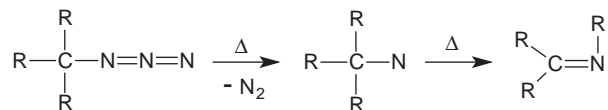
### 1,2-Migrations

The 1,2-shifts are more common for aryl, vinyl, acetoxy, and halogen migrating groups. The 1,2-migration involving free radicals is less common for hydrogen atoms, methyl groups, and even for shorter alkyl groups. However, migration of hydrogen and alkyl groups does occur for certain cases. A 1,2-shift with a methyl migration may take place during alcohol pyrolysis with water elimination when the  $\beta$ -carbons to the OH group do not contain any hydrogens. This reaction is assumed to be a Wagner–Meerwein type rearrangement (see reaction 9.1.16), although the carbocation presence has not been confirmed. An example of such methyl 1,2-migration in an alcohol is shown below:



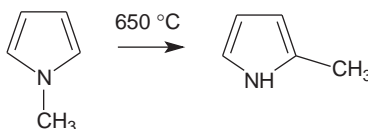
Pinacol rearrangement (see reaction 2.2.10) is also a typical case of 1,2-migration.

The formation of imines from alkyl azides is an example of 1,2-migration:



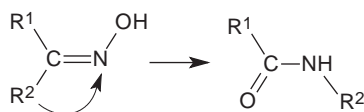
Acyl azides eliminate nitrogen and form isocyanates in a similar manner.

Another reaction that may appear to be a 1,2-migration is that of alkyl groups in pyrroles, indols, and imidazoles during pyrolysis [30]. This reaction for 1-methylpyrrole is presented as follows:

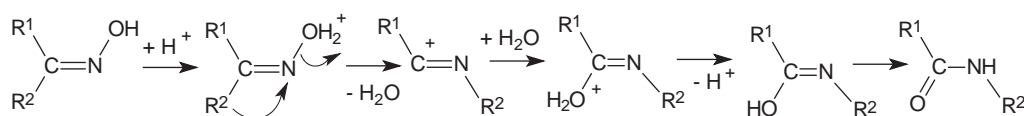


However, the methyl migration in *N*-methylpyrrol has a concerted mechanism and is, in fact, a [1,5] sigmatropic rearrangement.

Another rearrangement reaction encountered in oximes is Beckmann transposition, where oximes are transformed into substituted amides. This reaction usually takes place under the influence of some catalysts (e.g., strong Lewis acids like  $\text{AlCl}_3$ ,  $\text{BF}_3$ ). However, in the case of oxime salts with acids (e.g.,  $\text{HCl}$ ), the reaction occurs when the compounds are heated. The transposition takes place as shown below:

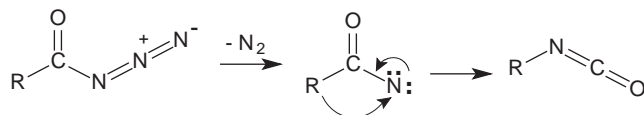


Only the group in *trans* (usually indicated as *anti*) to the hydroxyl is the one that migrates. In case of oxime hydrochlorides, the reaction mechanism is probably the following:



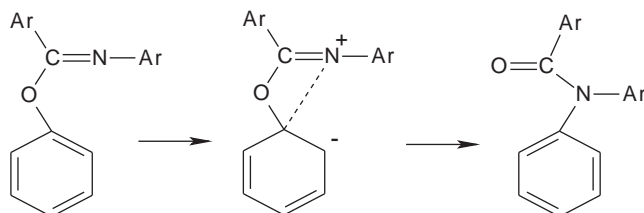
An interesting type of 1,2-migration during pyrolysis is that occurring in certain heterocyclic compounds that undergo migration of the heteroatom (typically with low yield). Examples include the formation of low levels of isoquinoline during quinoline pyrolysis and the formation of pyrimidine during the pyrolysis of pyrazine.

A 1,2-migration occurs during thermal decomposition of azides (Curtius rearrangement). In this reaction, an azide eliminates  $\text{N}_2$  and generates an isocyanate as shown in the reaction below:



The migration of a substituent from the carbon to nitrogen is also seen in Lossen rearrangement of hydroxamic acids into isocyanates (see Section 19.8).

Chapman rearrangement is another transformation of a nitrogenous compound as a result of heating. In this reaction, an aryl imino ether is changed into an amide:

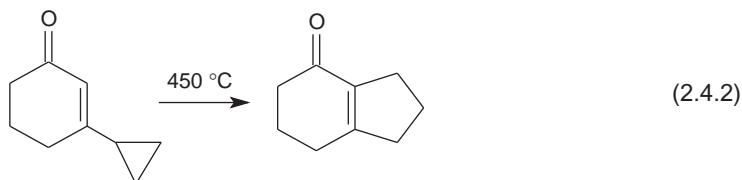


### Rearrangements in compounds with bent bonds

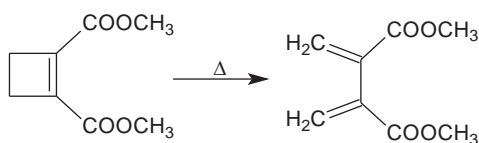
The  $\text{sp}^3$  orbital overlapping for carbon compounds is maximized when the bond angles are  $109.5^\circ$ . When the angle between the bonds deviates from this value, the stability of these bonds is decreased (this can be indicated as having bent bonds). The modification of the bond angle occurs, for example, in certain cyclic compounds. The bonds involving heteroatoms also have an optimum value, and

heterocyclic compounds can display bent bonds. The thermal stability of compounds with bent bonds (such as strained cycles) is, in general, low, and upon heating they have the tendency to form more stable compounds, frequently through rearrangements.

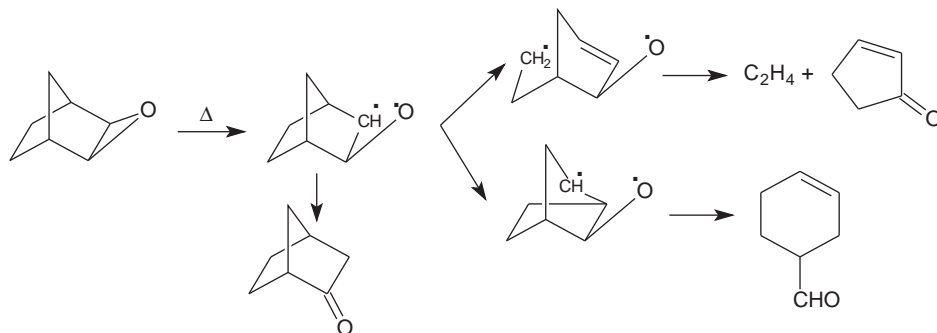
Among the cycles that easily undergo rearrangements are the cyclopropanes, cyclobutanes, and the azirines. An example is 2-cyclohexen-3-cyclopropyl-1-one, which changes into 2,3,5,6,7-pentahydroinden-4-one [31]:



The rearrangement for a cyclobutane derivative is exemplified for cyclobutane-1,2-dicarboxylic acid dimethylester [32]:



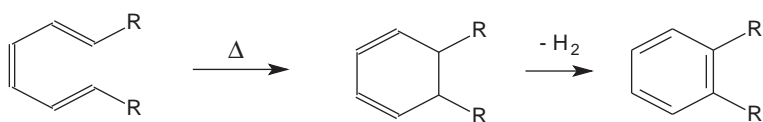
Another example of bent bond compound rearrangement is that encountered in epoxide pyrolysis. The mechanism of this rearrangement seems to involve a diradical formation, and, for a compound such as norbornene epoxide, the reaction occurs as follows [33]:



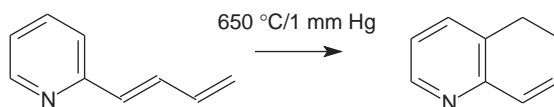
Other mechanisms may also be followed during the rearrangement of compounds with strained cycles such as a concerted mechanism [34].

### Electrocyclic rearrangements

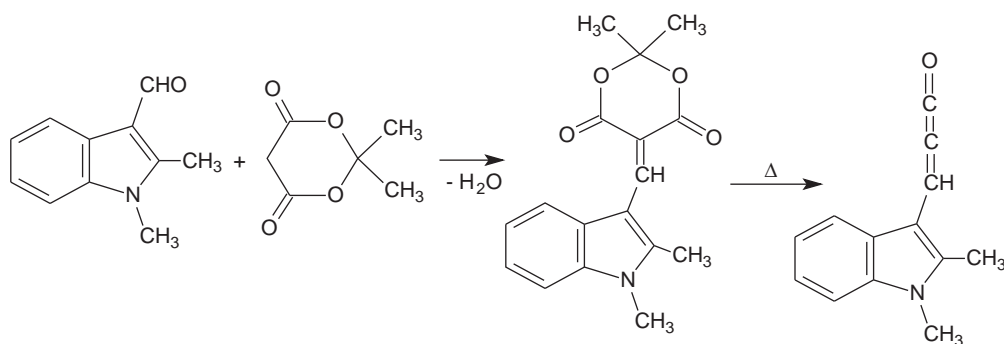
Compounds containing a system of six  $\pi$  electrons typically form by pyrolysis dihydroaromatic compounds, and, if possible, by a subsequent elimination reaction they form aromatic compounds. A common case for this type of rearrangement is that of the conversion of 1,3,5-trienes into 1,3-cyclohexadienes, which can occur during pyrolysis:



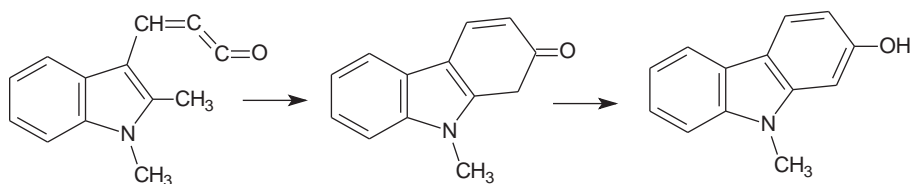
From among many examples of this reaction reported in the literature [34], the formation of 5,6-dihydroquinoline from 2-(1,3-butadienyl)pyridine is shown below:



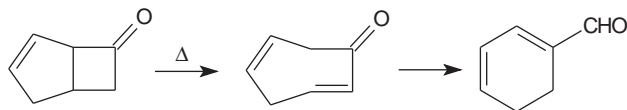
Electrocyclic rearrangement has applications in organic synthesis of naphthols and other hydroxyaromatic compounds [35]. The synthesis makes use of Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) following a condensation with a desired aldehyde and pyrolysis of the arylmethylene derivative [34]. One such chain of reactions for the synthesis of *N*-methyl-2-hydroxycarbazol [36] is the following:



The substituted methyleneketene generated during pyrolysis undergo electrocyclic rearrangements as follows:



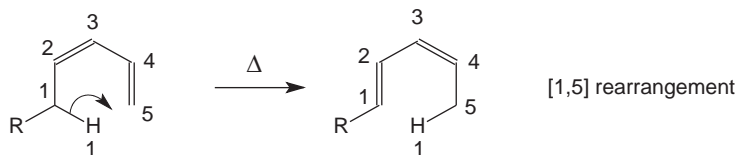
Other reactions of this type occur, for example, for compounds with cycles different from six atoms that change into more stable six-atom rings, as shown in the following example for bicyclo[3.2.0]hept-3-en-6-one [34]:



### Sigmatropic rearrangements

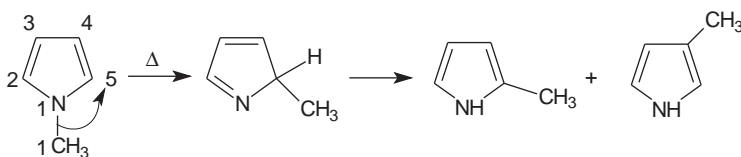
Sigmatropic rearrangements are common in pyrolytic reactions, and their end result is the migration of a  $\sigma$  bond. The 1,5-migration of hydrogen, for example, takes place in many reactions above 200–300 °C.

This migration can be written schematically as follows:



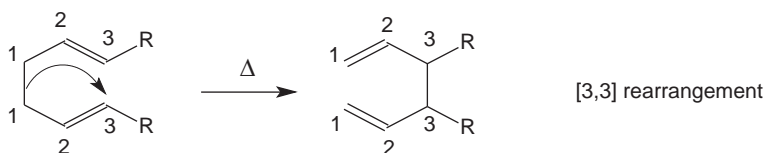
The order  $[i,j]$  of the sigmatropic reaction is determined by counting the atoms over which end the  $\sigma$  bond has moved, starting with 1,1 at the initial position of each end of the  $\sigma$  bond [2]. The [1,5] shifts in pyrolytic reactions are common not only for hydrogen, but also for alkyl, aryl, and acyl groups.

The [1,5] sigmatropic rearrangements can include the migration of the alkyl group during the pyrolysis of alkyl pyrroles, as shown below:

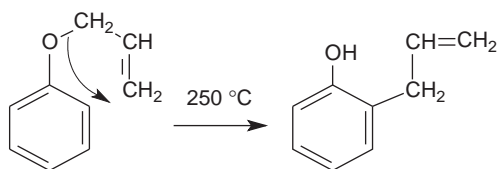


As in many pyrolytic reactions, the above migration is not the only reaction that occurs during the heating process of methylpyrrole. Other reactions are also associated with the migration.

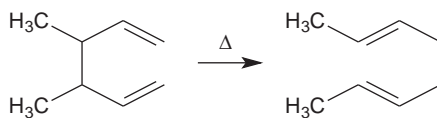
Among other sigmatropic reactions, the [3,3] rearrangements are also common. This type of rearrangement takes place as follows:



A typical [3,3] sigmatropic shift takes place during Claisen rearrangements, shown below for allyl phenyl ether:



When the alkyl groups are subject to a [1,5] shift and move along a 1,5-diene chain, the reaction is known as Cope rearrangement. This reaction is shown below for 3,4-dimethyl-1,5-hexadiene:

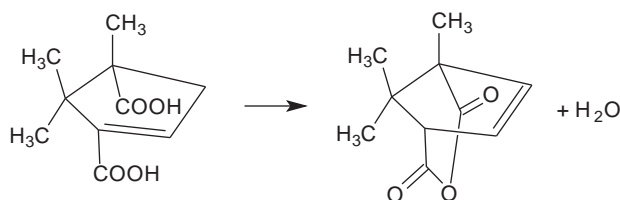


Other examples of rearrangements that occur during pyrolysis will be included in Part 2 of this book.



### Double bond migrations

In some pyrolytic reactions, a migration of a double bond has been noticed. One such example is seen during the formation of an anhydride from dehydrocamphoric acid in the reaction shown below:



The migration of the double bond follows the empirical observation (Bredt's rule [5]) indicating that a double bond cannot be placed at the bridgehead of a bridged ring system. The migration of double bonds frequently is seen when more stable conjugated systems are formed from compounds already containing double bonds. Some examples of this type of migration will be shown in Part 2 of this book.

### Steric changes during pyrolytic reactions

The molecules involved in pyrolytic reactions are subject to energies (temperatures) capable of breaking covalent bonds and increasing reaction rates with many orders of magnitude. For this reason, steric changes do occur during pyrolysis. However, for some compounds, the area with a specific steric structure is not affected by pyrolysis. Also, as indicated, for example, in the case of pyrolytic eliminations (see Section 2.2), in some cases there are specific rules regarding the steric characteristics of the parent molecule that are followed for a specific reaction.

For molecules that contain double bonds and for which *cis*-, *trans*- (*Z*, *E*) isomers are possible, it is common that during pyrolysis the initial molecule suffers isomerization and the fragments containing the steric moiety do not preserve the initial structure. As an example, pyrolysis of coniferyl alcohol is discussed further. The compound is found in nature mainly as its *E*-isomer. By pyrolysis, along with smaller fragments of the parent molecule, a mixture of undecomposed *E*-isomer (*trans*) and an equal amount of *Z*-isomer are present in the pyrolysate. This is illustrated in Figure 2.4.1, which shows a 2-min

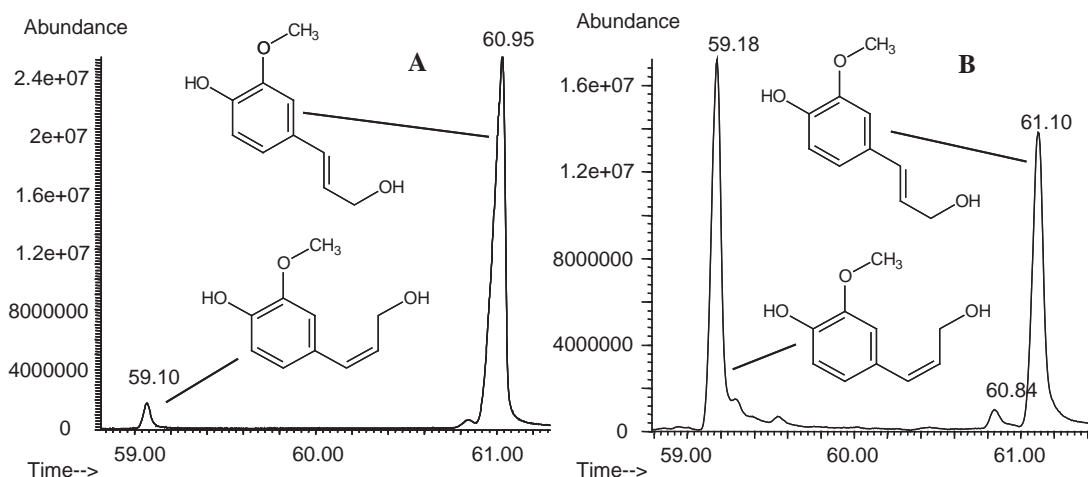
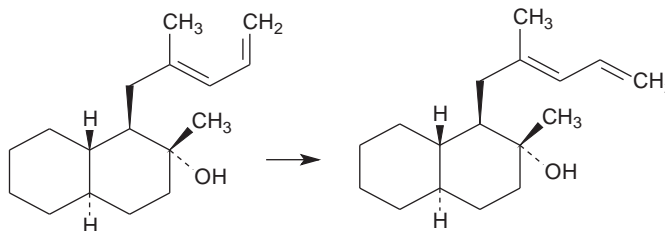


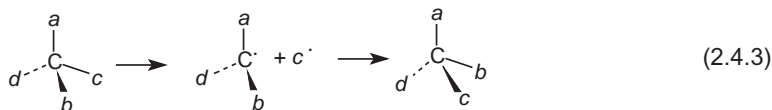
FIGURE 2.4.1. (A) Time window between 59 min and 61 min showing the peak of *trans*-coniferyl alcohol (60.95 min) and a trace of *cis*-coniferyl alcohol (59.00 min). (B) The same time window in the pyrogram of coniferyl alcohol showing the undecomposed compound (61.10 min) and its *cis* isomer (59.18 min).

window from the chromatogram of a solution of the parent compound (Figure 2.4.1A) and the same time window from the chromatogram of the pyrolysate (pyrogram) (Figure 2.4.1B). The first peak in the two chromatograms (59.10 and 59.18 min, respectively) belongs to the *Z*-isomer, and the second peak (60.95 and 61.10 min, respectively) belongs to the *E*-isomer. Initially, the *Z*-isomer is present only as an impurity, but during pyrolysis (at 900 °C), a certain amount of *E*-coniferyl alcohol is changed into its *Z*-isomer.

Similarly, other compounds generate the more stable *trans* (*E*) compound from the *cis* compound when heated. This type of transformation is shown as an example for the transformation of *cis*-abienol into *trans*-abienol when heated around 250 °C [37].



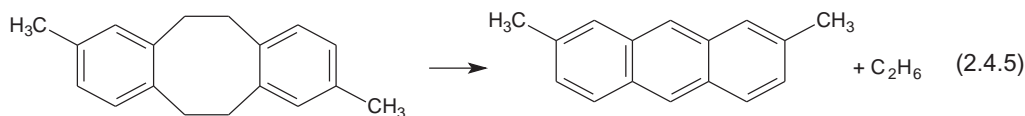
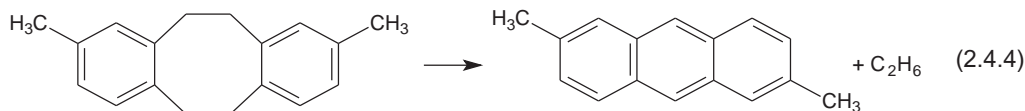
Regarding the preservation of chirality from the parent molecule into the fragments that inherit the chiral center, it can be assumed that without the migration of a group, the chirality is preserved. However, during pyrolysis, reactions of the type:



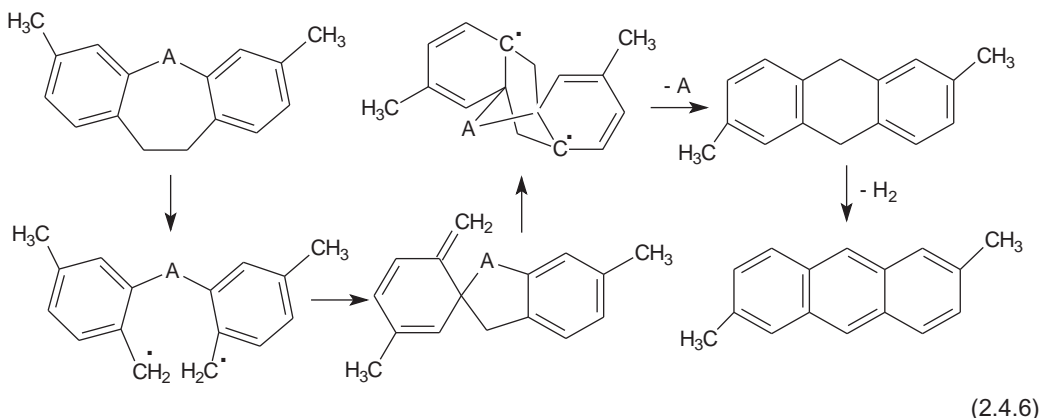
are possible and the end result is a mixture of enantiomers. There is very little information about this type of process [34]. Typical analytical procedures applied for the analysis of pyrolysates, such as those using GC separations, are not able to distinguish between enantiomers except when special chiral columns are used. However, the use of chiral columns is not a common practice in the analysis of pyrolysates.

In some cases, the steric configuration of the parent molecule is critical for the pyrolysis outcome. This is, for example, the case for carbohydrates [38]. From these compounds, in addition to smaller molecules, anhydro sugars are formed during pyrolysis. These anhydro sugars retain some of the chiral carbons of the parent molecule, and formed diastereoisomers of the same compound from different sugars (see Chapter 16).

Many other pyrolytic reactions lead to regiospecific products. As an example, 2,9-dimethyl-5,6,11,12-tetrahydrido[*a,e*] [8]annulene generates by pyrolysis 2,6-dimethylantracene, while 2,8-dimethyl derivative of the annulene generates 2,7-dimethylantracene as shown below [39]:



The formation of regiospecific anthracene derivatives from dibenzoannulenes is a more general reaction, and its mechanism is shown as follows [39]:



where  $-A-$  can be:  $-\text{CH}_2-$ ,  $-\text{CH}_2\text{--CH}_2-$ ,  $-\text{CO}-$ ,  $-\text{CH}(\text{OH})-$ ,  $-\text{CH}(\text{CH}_2\text{OH})-$ , etc. [40–42].

## 2.5. OTHER REACTION TYPES IN PYROLYSIS

### General aspects

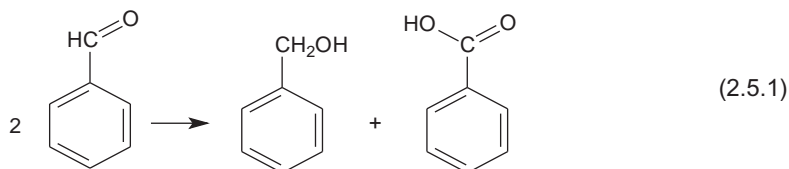
Besides the types of reactions previously described, which are more common in pyrolytic processes, some other chemical reactions can be seen in certain pyrolytic processes. Among these are reactions for organic compounds such as oxidations, reductions, substitutions, and additions. Sometimes, these reactions can be the first step in the pyrolysis, being caused by the higher reaction rates as a result of increased temperature. However, more commonly, these reactions follow an initial step that produces a fragmentation, a rearrangement, or an elimination.

### Oxidations/reductions

The oxidation/reduction reactions, defined as an increase/decrease in the oxidation number, cannot be applied directly in organic chemistry. This is due to the difficulty of defining the oxidation number for organic compounds where C–C bonds are present. For example, the carbon in pentane, considering the hydrogens as having a positive charge and carbons a negative charge, has the formal oxidation number  $-2.4$ , while in methane it is  $-4$ . For this reason, an “approximate” oxidation number must be assigned to each compound more or less arbitrarily. The assigned oxidation number of carbon is  $-4$  in saturated hydrocarbons; is  $-2$  in alkenes, alcohols, mono-chlorinated aliphatic hydrocarbons, and amines; is  $0$  in compounds with triple bonds, aldehydes, ketones, diols, etc.; is  $+2$  in acids, amides, and trichlorinated aliphatic hydrocarbons; and is  $+4$  in  $\text{CO}_2$  and  $\text{CCl}_4$ . Using this arbitrary assignment, the common definition for oxidation/reduction can be applied.

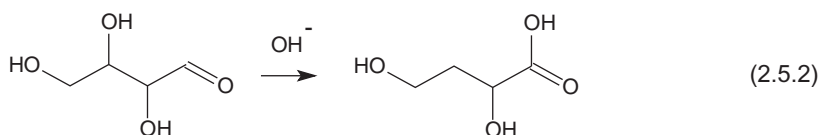
The changes in the oxidation number of carbon atoms in pyrolytic reactions are common. For example, hydrogen elimination is a typical oxidation reaction that takes place in pyrolysis. An oxidation/reduction reaction seen sometimes during pyrolysis, but more frequently during thermally assisted hydrolysis and methylation (see Section 2.6), is the transformation of aldehydes into an acid and an alcohol. This oxidation/reduction is known as Cannizzaro reaction when it is applied

to aromatic aldehydes:



Cannizzaro reaction is typically catalyzed by bases ( $\text{OH}^-$ ).

In strong basic medium, hydroxyaldehydes can be changed into acids in an oxidation/reduction reaction seen during thermally assisted hydrolysis and methylation of carbohydrates, as shown below for a tetrose, which can be changed into a saccharinic acid (deoxyaldonic acid) [43]:



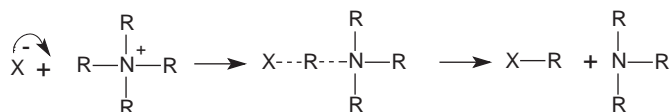
Some other oxidations or reductions may take place during pyrolysis as a subsequent reaction to the initial process. Certain free radical substitutions that involve the transfer of a hydrogen atom can also be considered oxidation/reduction reactions. However, the oxidation/reductions that take place in these reactions are not viewed as such, and other aspects of the reaction are used for their classification. On the other hand, the oxidation due to the presence of oxygen (intended or accidental) that may take place during pyrolysis (below ignition temperature) or reductions due to the addition of hydrogen during pyrolysis are labeled as oxidations or reductions.

### Substitutions

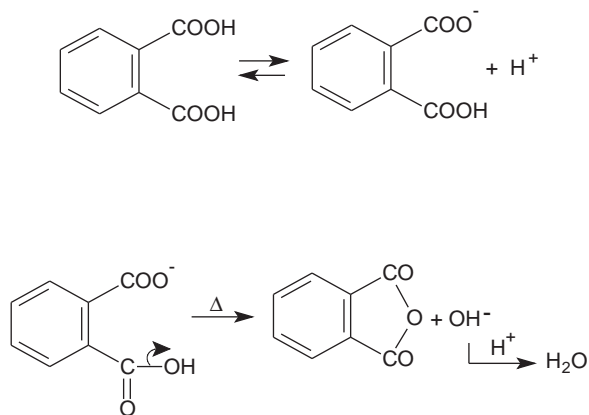
Either as a first step of pyrolysis or as a result of the interaction of molecules resulting from previous pyrolysis steps, substitutions and additions are common reactions during the pyrolytic process. The increased reaction rate due to the high temperature in pyrolysis makes many reactions of this type possible. The nucleophilic substitution takes place with the attack of a reagent that brings an electron pair to the substrate. This pair is used to form a new bond. The leaving group retains its electron pair. The general scheme of this type of reaction can be written as follows:



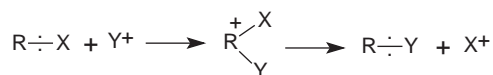
The nucleophile  $\ddot{\text{Y}}$  can be neutral or negatively charged, and the reaction may have bimolecular ( $\text{S}_{\text{N}}2$ ), unimolecular ( $\text{S}_{\text{N}}1$ ), or other mechanisms. Since the first step in pyrolysis typically starts with one single molecular type of reaction, nucleophilic substitutions may occur as a reaction between two components in the pyrolysate after the first step of decomposition or when a part of the molecule acts as a nucleophile. This is the case, for example, in the case of pyrolysis of quaternary ammonium salts. The mechanism of this decomposition is shown below:



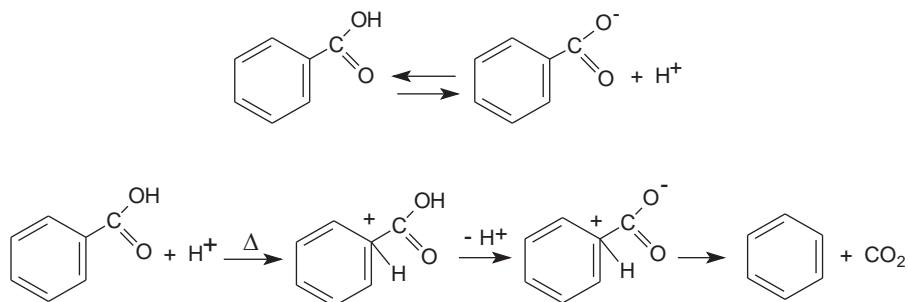
Another example of nucleophilic substitution is the formation of anhydrides during the pyrolysis of carboxylic acids. This is shown for a dicarboxylic acid, where the formation of a five-, six-, or seven-atom ring is critical for the anhydride formation:



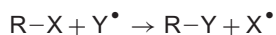
In electrophilic substitutions, the attacking species is an electrophile, typically a positive ion, with the reaction taking place as shown below:



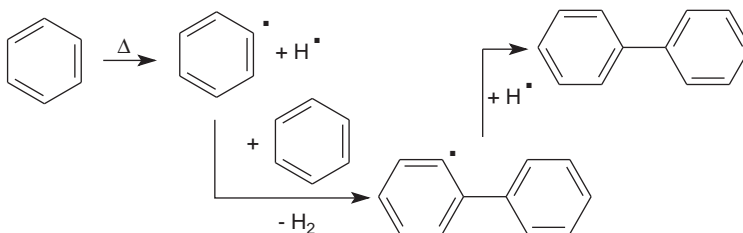
Similarly to other substitutions, the reaction takes place involving two components. For this reason, these reactions take place either involving a single molecular species that has two different moieties able to interact or after different compounds are formed in an initial pyrolysis step. The decarboxylation of aromatic acids can be viewed as an electrophilic substitution. This reaction is not uncommon during pyrolysis. For example, the decarboxylation of benzoic acid takes place as follows:



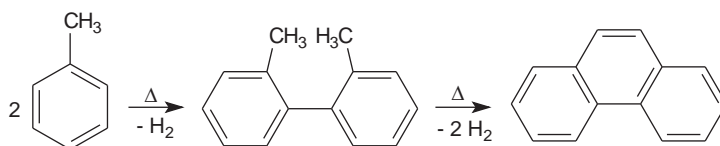
Free radical substitutions are also known to occur in pyrolytic reactions. A free radical substitution takes place as follows:



An example of this type of reaction is the formation of biphenyl from benzene at 700 °C (this reaction can be viewed as an oxidation because of the hydrogen elimination):



For substituted benzenes, a free radical substitution leads to polycyclic aromatic hydrocarbon, as shown for the formation of phenanthrene:

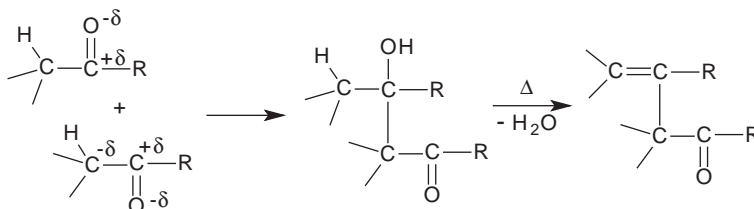


Polycyclic aromatic hydrocarbons with a higher number of condensed cycles can be generated by the same mechanism.

### Additions

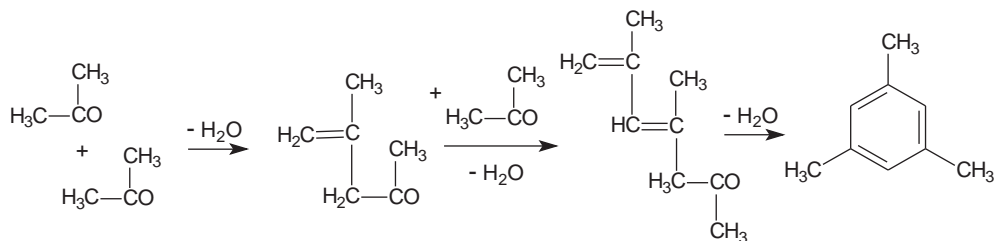
Additions to a double or triple bond or to a cyclopropane ring may take place in pyrolysis, although this type of reaction typically requires two molecular species to interact. In these reactions, it is common that the molecule containing the double bond is attacked by a nucleophile, an electrophile, or a free radical. Simultaneous attack with a four-center mechanism is also possible. Additions to conjugated systems are also common, for example, in Diels–Alder reactions.

For pyrolysis starting with a single molecular species, additions are possible if a part of the molecule acts as a double (or triple) bond carrier and another part acts as the reagent. This is, for example, the case of aldol condensation, which takes place as follows:

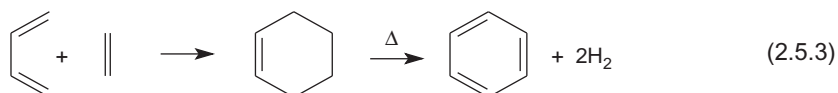


The reaction typically takes place with a basic catalyst. Under the influence of heat, the hydroxyaldehyde (aldol) or the hydroxy ketone eliminates water. A reaction of this type may explain

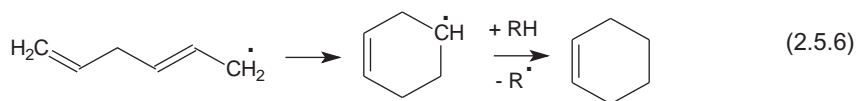
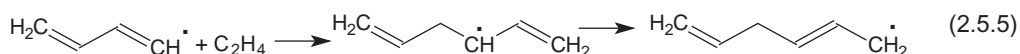
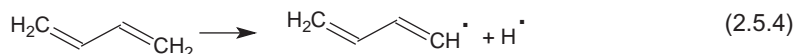
the formation of 1,3,6-trimethylbenzene in the pyrolysis of acetone, as shown below:



Addition reactions following the first step of pyrolysis are more common. This type of reaction may explain, for example, the formation of benzene (or other aromatic hydrocarbons) following the radicalic elimination during the pyrolysis of alkanes. In these reactions, the first step is the formation of unsaturated hydrocarbons, including some with multiple double bonds. When dienes are formed, they may react with alkenes in a Diels–Alder condensation. The resulting molecules can undergo further hydrogen elimination. This sequence of reactions is shown below:



However, the high temperature is not typically favorable for Diels–Alder condensation (see retro-Diels–Alder reactions) [44]. As temperature increases, the entropic component of the free energy makes condensations unfavorable (see Chapter 3). Alternatively, the result of reaction 2.5.3 can be achieved by a radicalic mechanism as shown below [45]:



Various other examples of similar reactions will be given in Part 2 of the book.

## 2.6. PYROLYSIS IN THE PRESENCE OF ADDITIONAL REACTANTS OR WITH CATALYSTS

### General aspects

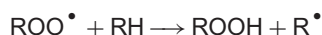
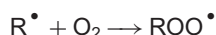
Pyrolytic reactions, mainly for analytical purposes, are frequently conducted in a helium atmosphere. However, analytical pyrolysis is not limited to the use of pyrolysis for the identification of an initial compound based on its pyrolysate composition. For a variety of studies, pyrolysis is performed in the presence of additional reactants or catalysts. Among the most common reagents are oxygen, water, and hydrogen. Even for analytical purposes, some specific reagents can be added. One common class of such reagents is the quaternary *N*-alkyl (or aryl) ammonium hydroxides that are used for the pyrolytic

alkylation of compounds with active hydrogens (such as acids) and for pyrolytic transesterifications used on esters such as glycerides.

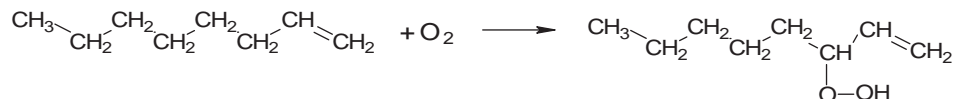
Oxygen from air sometimes is present unintentionally during pyrolysis or may be added to simulate burning. A true pyrolysis in the presence of oxygen (pure or in a mixture with other gases such as in air) should take place with a first step of thermal decomposition, followed by the reaction of oxygen with the pyrolysis products. In most cases, because the temperature of ignition of the organic compounds is exceeded by the pyrolysis temperature, the compounds burn when the oxygen is present above a given concentration.

### Pyrolysis in the presence of oxygen

Free oxygen has an unusual molecule. In its ground state, each of the two highest occupied molecular orbitals, which are degenerated, contain unpaired electrons (a triplet state of the molecule). This means that ordinary oxygen has the properties of a diradical. Although not extremely reactive, this diradical will react rapidly with many other radicals in a chain oxidation as follows:



If a pyrolysis reaction generates free radicals (see Section 2.2), the formation of hydroperoxides is likely. The new free radicals that are formed continue the reaction. In addition to the reaction with the free radicals formed during pyrolysis, the oxygen may also react at the elevated temperature with the initial compound that is subject to pyrolysis. An example of such reaction is shown as follows:



The hydroperoxide formed decomposes further under the influence of heat, reacting with other molecules and forming, for example, alcohol molecules.

In an excited electronic state, singlet oxygen is much more reactive. The oxygen in a singlet state can be generated by a photochemical reaction and may react with a wide variety of materials by autoxidation. The singlet oxygen may react with the double bond forming a dioxetane intermediate:



Various substances when exposed to air and light may contain oxidized groups such as peroxides (OOR). The O—O bond in peroxides is weak (30–50 kcal/mol) and, upon heating, dissociates to form free RO radicals and radical chains. These radicals may influence the composition of the pyrolysis products. It is important, therefore, to consider this possibility when evaluating the composition of the pyrolysis products of a material that was exposed to air and light although the pyrolysis is performed in an inert gas.

Combustion is another process that commonly occurs during experiments involving pyrolysis in oxygen. The main reaction products resulting from combustion depend on the composition of the combusted material. For many organic compounds containing only carbon, hydrogen, and oxygen, the main combustion products are CO<sub>2</sub>, CO, and H<sub>2</sub>O. For other compounds containing elements such as nitrogen, sulfur, halogens, phosphorus, etc., a variety of other substances are formed during combustion. The combustion occurring before or in parallel with pyrolysis has several effects on



pyrolysis results. One effect is the consumption of the initial material, the amount of substance undergoing true pyrolysis being smaller than the initial amount taken for the experiment. When attempting mass balance for the pyrolysis experiment, this factor may become very important. The yields of a pyrolytic process should always take into account the potential burning of a part of the material used for pyrolysis.

### ***Pyrolysis in the presence of hydrogen***

Hydrogen can react with numerous chemical compounds. However, molecular hydrogen as such is not very reactive. In most chemical reactions, only the hydrogen generated directly in the reaction medium is active (e.g., from Zn and HCl). Pyrolysis in molecular hydrogen proceeds in most cases in a manner similar to the pyrolysis in an inert gas (helium or nitrogen). In order to make use of the hydrogen reactivity, a catalyst must be used. Common catalysts are metals such as platinum or nickel. In analytical pyrolysis, hydrogen and a catalyst can be used [46] to diminish the number of species resulting from pyrolysis. When the pyrolytic process is followed by a chromatographic separation, the chromatogram of the pyrolysate (the pyrogram) can appear to be too complicated. If this pyrogram consists, for example, of groups of compounds with the same carbon chain but containing single and multiple bonds, this can be simplified by hydrogenation. For each group of substances, only the saturated compounds initially present or generated in the reaction will appear after a catalytic hydrogenation. The procedure can be useful only in some particular cases, and it is not commonly used.

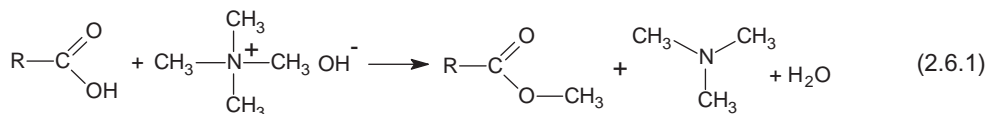
### ***Pyrolysis in the presence of water***

The presence of water as a reaction product from the pyrolytic processes or as adsorbed water on the material to be pyrolyzed is not unusual. However, in analytical pyrolysis, water is not commonly added to the sample. During some pyrolytic processes with industrial applications such as wood pyrolysis, water sometimes is added intentionally. The main effect of water during pyrolysis is hydrolysis. This takes place as the temperature elevates. The reproducibility in analytical pyrolysis may be influenced by the variability of water content of the initial sample [47].

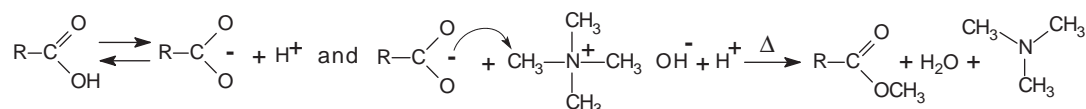
### ***Pyrolysis/alkylation***

One of the problems during the analysis of pyrolysates using chromatographic techniques is that polar compounds such as larger acids are not easily eluted from typical chromatographic columns. In situ derivatization is one of the solutions to this problem. Several attempts have been made to perform in situ silylation, but the results are still modest. The silylation reaction is not rapid enough, and a delay period between pyrolysis and analysis is usually necessary for the reaction to take place. Better results are obtained by performing pyrolysis in the presence of quaternary *N*-alkyl (or alkyl, aryl) ammonium hydroxides [43,48–52]. The procedure was initially applied by the addition of the reagent in the hot injection port of a gas chromatograph for the methylation of acidic components from a sample, and later with different pyrolytic techniques by directly adding tetramethyl ammonium hydroxide (TMAH) together with the material to be pyrolyzed [53,54]. The derivatization reagents are applied on the sample either as an aqueous solution (e.g., for TMAH) or as methanolic solutions. When this procedure is used in the pyrolysis of acids or of nonvolatile esters (such as triglycerides), the resulting pyrolysate contains methyl esters that are more volatile than the initial compounds. TMAH is not the only reagent used as a derivatization reagent during pyrolysis. Other quaternary *N*-alkyl (or alkyl–aryl) ammonium hydroxides are used successfully as derivatization reagents. Among these are tetrabutyl ammonium hydroxide [54], phenyltrimethylammonium hydroxide (or trimethyl anilinium hydroxide), and (*m*-trifluoromethyl-phenyl)trimethyl ammonium hydroxide (or trimethyl-trifluoro-*m*-tolyl ammonium hydroxide) [55]. Other similar pyrolytic derivatizations with the generation of esters having ethyl, propyl, hexyl groups, etc. are known.

The derivatization reaction can be applied to acids and also to other compounds that contain acidic hydrogens such as phenols and carbohydrates. The methylation reaction using TMAH is shown below for a monocarboxylic acid:

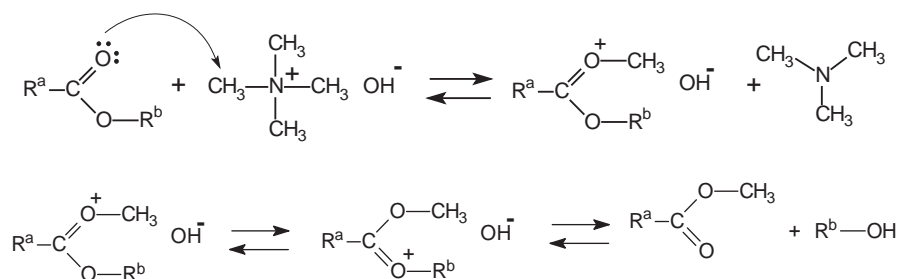


The mechanism of this reaction is a nucleophilic substitution as shown below:



During pyrolysis, some quaternary ammonium hydroxide is decomposed to form methanol and trimethylamine (see reaction 13.3.2). Other small molecules are also generated from the reagent, including dimethyl ether in the case of derivatization with TMAH, and anisole in the case of derivatization with phenyltrimethylammonium hydroxide.

Methylation derivatization has also been used successfully for the transmethylation of esters and carbonates. This reaction has been used, for example, in the analysis of triglycerides. For an ester, the reaction can take place by the following mechanism:



Although pyrolysis in the presence of TMAH generates methylated compounds, it has been shown that off-line methylation of the pyrolysis products is not identical to the products of pyrolysis in the presence of the methylating reagent [56]. Some hydrolysis type reactions or other reactions that do not occur in simple pyrolysis take place in the presence of TMAH or other tetraalkylammonium hydroxides. New reactions can take place in strong basic medium generated by these reagents. Other reactions besides thermal decomposition and methylation do not occur in the same manner for all samples. For example, acids and phenols show fewer unexpected reactions compared with the case of carbohydrates [57]. Particularly for carbohydrates, pyrolysis in the presence of TMAH is not equivalent with the methylation of the compounds generated from the simple pyrolysis, and the process is known as thermo chemolysis. In other cases, only part of the pyrolysate is methylated and other part remains unmethylated. The strong basic character of substituted ammonium hydroxide type reagents puts some limitations to their use. For this reason, the use of tetramethylammonium fluoride (TMAF), phenyltrimethylammonium fluoride, trimethyl(trifluorotolyl)ammonium hydroxide, or phenyltrimethylammonium acetate as pyrolytic methylation reagents without the additional effect of the basic character of TMAH is promising [56]. The pyrolysis in the presence of methylating/hydrolysis reagents such as TMAH is utilized more frequently during the pyrolysis of compounds that have acidic groups [58,59] or ester groups. In addition to the reagent itself, it has been shown that the solvent for TMAH may play a role in the reaction during pyrolysis. The use of deuterated methanol as a solvent for TMAH showed that the solvent is involved in a methanolysis process [60].

### Pyrolysis in the presence of catalysts

An example of the use of a catalyst together with  $H_2$  as a reagent gas during pyrolysis was indicated previously [46]. The catalysts can be added on purpose, or they may be present inadvertently in the sample. Compounds such as  $SiO_2$  or  $Al_2O_3$  can play the role of a catalyst in some decomposition reactions. Even carbon was shown to have a catalytic effect during the decomposition of certain polymers [61]. The influence of  $SiO_2$  and of  $Al_2O_3$  on the pyrolysis of nicotine is illustrated in Figures 2.6.1 and 2.6.2, respectively. The pyrograms were obtained from 0.05 mg nicotine on 1 mg support of  $SiO_2$  and  $Al_2O_3$ , and the pyrolysis was performed in helium at  $700^\circ C$ . The analysis of the pyrolysates was performed online by GC/MS using identical experimental conditions for both pyrograms.

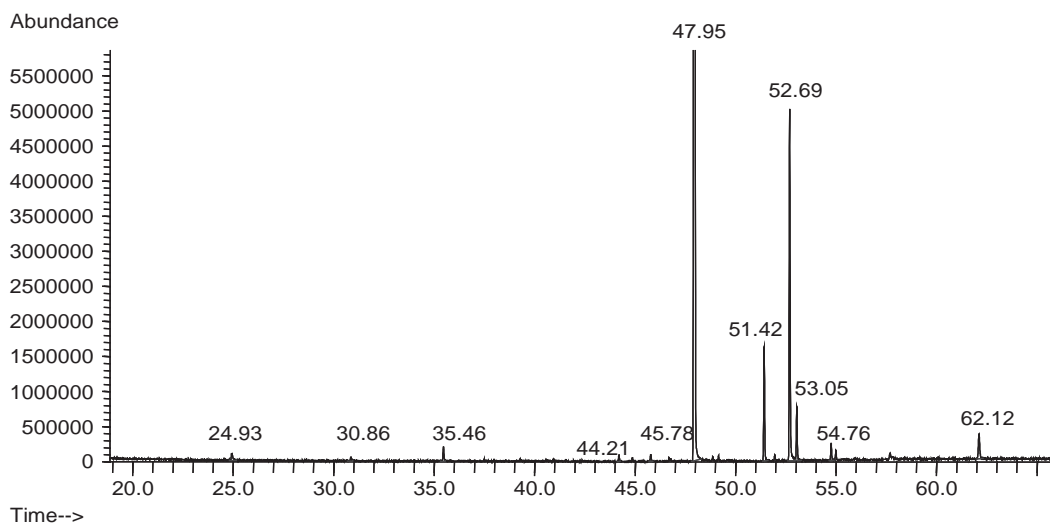


FIGURE 2.6.1. Pyrogram obtained from 0.05 mg nicotine on a  $SiO_2$  support in helium at  $700^\circ C$ . Peak identification given in Table 2.6.1.

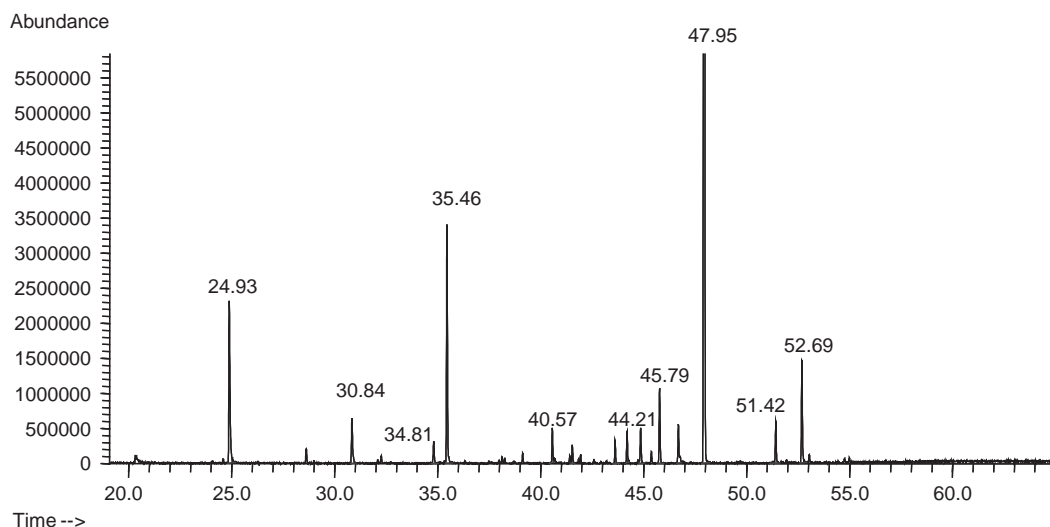


FIGURE 2.6.2. Pyrogram obtained from 0.05 mg nicotine on an  $Al_2O_3$  support in helium at  $700^\circ C$ . Peak identification given in Table 2.6.1.

TABLE 2.6.1. List of compounds identified in the pyrolysates of nicotine on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> supports, including individual peak areas in the pyrograms

No.	Compound	MW	Formula	CAS no.	Ret. time	Area % on SiO <sub>2</sub>	Area % on Al <sub>2</sub> O <sub>3</sub>
1	3-Methyl-1H-pyrrole	81	C <sub>5</sub> H <sub>7</sub> N	616-43-3	24.57	0.01	0.14
2	Pyridine	79	C <sub>5</sub> H <sub>5</sub> N	110-86-1	24.887	0.03	4.52
3	1H-Pyrrole	67	C <sub>4</sub> H <sub>5</sub> N	109-97-7	28.622	0.00	0.39
4	3-Methylpyridine	93	C <sub>6</sub> H <sub>7</sub> N	108-99-6	30.841	0.02	1.24
5	2-Methyl-1H-pyrrole	81	C <sub>5</sub> H <sub>7</sub> N	636-41-7	32.263	0.00	0.19
6	3-Ethylpyridine	107	C <sub>7</sub> H <sub>9</sub> N	536-78-7	34.812	0.00	0.61
7	3-Ethenylpyridine	105	C <sub>7</sub> H <sub>7</sub> N	1121-55-7	35.455	0.37	5.21
8	2,3,5-Trimethyl-1H-pyrrole	109	C <sub>7</sub> H <sub>11</sub> N	2199-41-9	38.129	0.00	0.15
9	2,3-Dihydro-1H-indole	119	C <sub>8</sub> H <sub>9</sub> N	496-15-1	39.13	0.01	0.26
10	2,3-Cyclopentenopyridine	119	C <sub>8</sub> H <sub>9</sub> N	533-37-9	40.572	0.01	0.69
11	2,3,4,5-Tetramethyl-1H-pyrrole	123	C <sub>8</sub> H <sub>13</sub> N	1003-90-3	41.421	0.00	0.20
12	7-Methyl-5,6,7-trihydrocyclopenta[2,1- <i>b</i> ] pyridine?	133	C <sub>9</sub> H <sub>11</sub> N	N/A	41.543	0.00	0.47
13	2-Methyl-5-(1-methylethenyl)pyridine	133	C <sub>9</sub> H <sub>11</sub> N	635-46-1	41.955	0.00	0.26
14	3-(but-1-enyl)pyridine?	133	C <sub>9</sub> H <sub>11</sub> N	N/A	43.628	0.00	0.55
15	7-Methyl-1H-indole	131	C <sub>9</sub> H <sub>9</sub> N	933-67-5	44.207	0.21	0.69
16	4-Methyl-1H-indole	131	C <sub>9</sub> H <sub>9</sub> N	16096-32-5	44.867	0.01	0.89
17	5-Methyl-1H-indole	131	C <sub>9</sub> H <sub>9</sub> N	614-96-0	45.385	0.00	0.37
18	Quinoline	129	C <sub>9</sub> H <sub>7</sub> N	91-22-5	45.788	0.22	1.76
19	Isoquinoline	129	C <sub>9</sub> H <sub>7</sub> N	119-65-3	46.697	0.01	0.76
20	3-(1-Methyl-2-pyrrolidinyl)pyridine (nicotine)	162	C <sub>10</sub> H <sub>14</sub> N <sub>2</sub>	54-11-5	47.949	85.63	76.88
21	3-(3,4-Dihydro-2H-pyrrol-5-yl)pyridine (myosmine)	146	C <sub>9</sub> H <sub>10</sub> N <sub>2</sub>	532-12-7	51.422	2.60	1.02
22	1H-Indazole	118	C <sub>7</sub> H <sub>6</sub> N <sub>2</sub>	271-44-3	51.951	0.18	0.13
23	3-(1-Methyl-1H-pyrrol-2-yl)pyridine (β-nicotyrine)	158	C <sub>10</sub> H <sub>10</sub> N <sub>2</sub>	487-19-4	52.69	7.67	2.50
24	1,4-Dimethyl-2-phenylimidazole?	172	C <sub>11</sub> H <sub>12</sub> N <sub>2</sub>	N/A	53.048	1.26	0.26
25	1,4-Dimethyl-5-phenylimidazole?	172	C <sub>11</sub> H <sub>12</sub> N <sub>2</sub>	62576-11-8	54.759	0.40	0.02
26	3-Pyrrol-2-yl-pyridine	144	C <sub>9</sub> H <sub>8</sub> N <sub>2</sub>	494-98-4	57.691	0.59	0.00
27	1-Methyl-5-(3-pyridinyl)-1,2-pyrrolidinone (cotinine)*	176	C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> O	486-56-6	62.09	0.87	0.00

\*The formation of cotinine is probably caused by the presence of traces of oxygen in the pyrolytic atmosphere.

The identification of various peaks in the pyrograms, as obtained by searching the NIST v. 2.0a mass spectral library, is given in Table 2.6.1.

As shown in Figures 2.6.1 and 2.6.2 and in Table 2.6.1, the composition of the resulting pyrolysates on  $\text{SiO}_2$  or on  $\text{Al}_2\text{O}_3$  supports shows differences. More nicotine is decomposed on  $\text{Al}_2\text{O}_3$  than on  $\text{SiO}_2$ , and, when present in both pyrolysates, the amount of each decomposition product is not the same from one support to the other.

Catalytic pyrolysis is widely used for various practical purposes, particularly during the pyrolysis of hydrocarbons related to oil processing. Various examples of the use of catalysts during pyrolysis are given in Part 2 of this book.

Catalytic effects during pyrolysis may also occur unintentionally during the burning of composite materials. For example, wood, coal, city waste, etc. contain inorganic compounds that are transformed into oxides or silicates during the burning process. These solid inorganic substances may influence the outcome of the pyrolysis process associated with burning.

## 2.7. PYROLYSIS OF MIXTURES OF COMPOUNDS

### *General aspects*

Pyrolysis of mixtures of compounds is a complex problem, numerous parameters being involved in determining the outcome of the process. Both physical parameters, such as experimental conditions in which pyrolysis takes place, and chemical parameters affect the pyrolytic outcome. The nature of the participating compounds as well as the pyrolysis mechanism are important factors, and the result of pyrolysis is a combined effect of physical and chemical factors. A few examples of added compounds influencing the pyrolysis of other compounds were given in Section 2.6, where it was shown that reagents could be added by purpose to influence the pyrolysis outcome. Other examples are given in Part 2 of this book.

In the case of industrial pyrolysis performed on natural mixtures, a separation of the components to be pyrolyzed may not be economical. Many examples of pyrolysis of mixtures are encountered in the oil industry (see, e.g., [62]). One such example is the addition of heavier hydrocarbons during pyrolysis of ethane to influence the formation of ethylene. It was found that the presence of heavier hydrocarbons accelerates the decomposition and ethylene formation at moderate ethane conversions. The same addition has the opposite effect at higher conversions [63]. Alkenes addition decreases the reaction rate of ethane decomposition.

Pyrolysis of solid samples consisting of more than one component, particularly performed in flash mode, may occur with little influence between the sample components when the pyrolysate does not contain highly reactive species or contains species that do not have the potential to interact. This is the case of many compounds that can be pyrolyzed together with little interference. However, when there is potential for the pyrolysis products to interact, the pyrolysate composition is affected by the composition of the mixture. This interaction complicates significantly the result of pyrolysis of mixtures, since some compounds are affected while others may remain unmodified. This type of effect is illustrated below by pyrolysis of a mixture of glucose and isoleucine. The pyrolysis was performed in flash mode at 900 °C, and the resulting pyrolysate was analyzed online by a GC/MS technique, generating chromatograms of the pyrolysate (pyrograms) shown in Figure 2.7.1. The pyrogram of pure glucose (Glu) is shown in Trace A, and that of pure isoleucine (Ile) is shown in Trace E. Figure 2.7.1 also shows the pyrograms of mixtures of the two compounds in the mole ratios Glu:Ile = 3:1 (Trace B), Glu:Ile = 1.45:1 (Trace C), and Glu:Ile = 0.36:1 (Trace D).

The main compounds in glucose pyrolysate include  $\text{H}_2\text{O}$  (not shown in the pyrogram),  $\text{CO}_2$  (Ret. time 4.06 min), formaldehyde (Ret. time 4.45 min), hydroxyacetaldehyde (Ret. time 17.39 min), 1,4-dioxadiene (Ret. time 28.63 min), furfural (Ret. time 30.11 min), 5-hydroxymethylfurfural (Ret. time 47.42), levoglucosan (Ret. time 56.36), and 1,6-anhydro- $\beta$ -D-glucofuranose (Ret. time 59.68 min). (See also Figure 16.1.5 and Table 16.1.2 for glucose pyrolysis. The retention times from Figure 16.1.5 are longer with about 0.3 min compared to those from Figure 2.7.1A.) The pyrolysate of isoleucine contains mainly 2-methylbutanal (Ret. time 18.00 min), 1-butaneamine-2-methyl-N-(2-methylbutylidene)

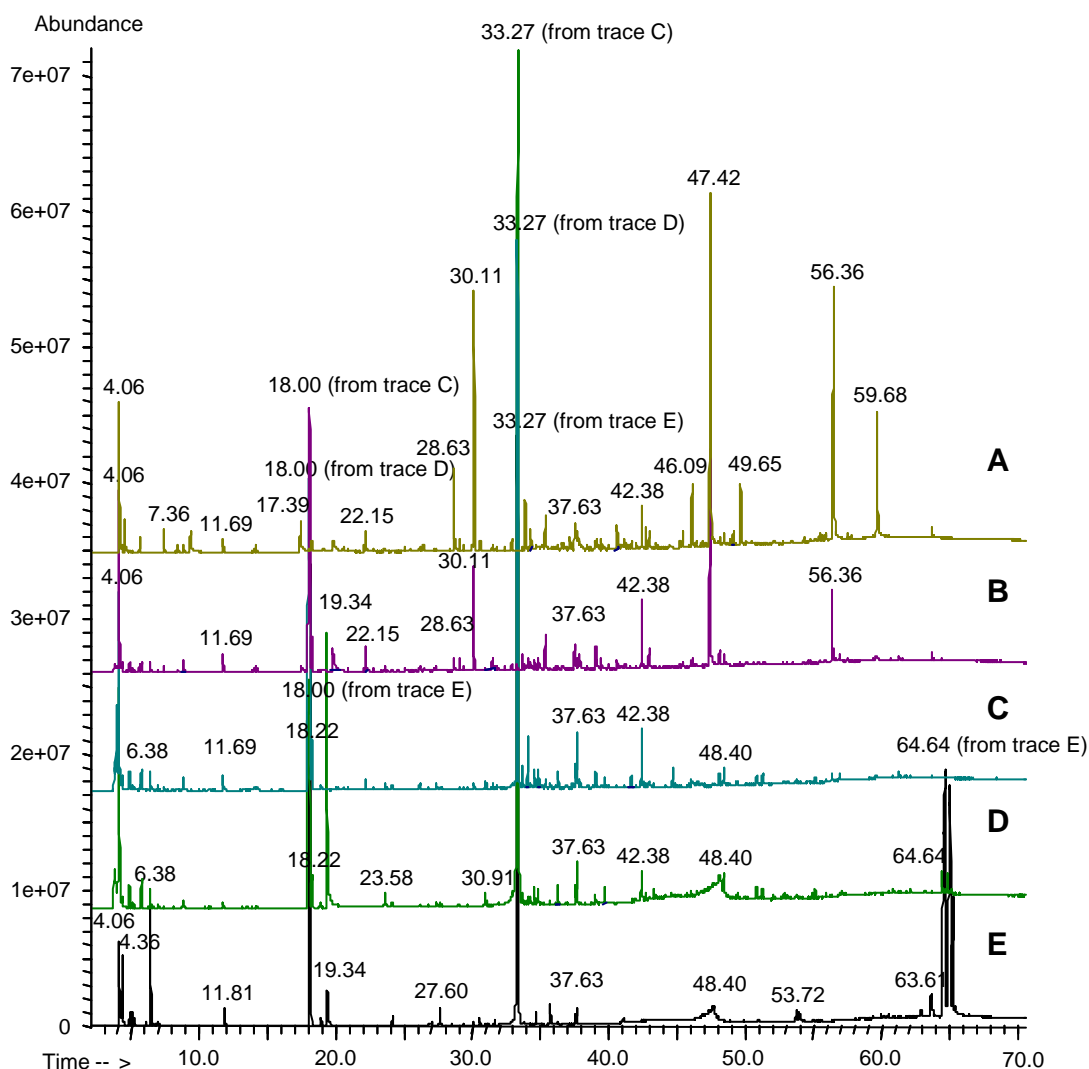


FIGURE 2.7.1. Pyrogram of *D*-(+)-glucose (Trace A), isoleucine (Trace E), and mixtures of the two in different proportions (Traces B, C, D) at 900°C.

(Ret. time 33.27 min), and 3,6-(2-methylpropyl)-2,5-diketopiperazine (Ret. time 64.64 min). (See also Figure 18.1.4 and Table 18.1.5 for isoleucine pyrolysis.)

Although Traces B, C, and D were generated from mixtures of glucose and isoleucine (in different proportions), it can be seen that some key compounds from either glucose or from isoleucine pyrolysates are missing. For example, furfural, 5-hydroxymethylfurfural, levoglucosan, and 1,6-anhydro- $\beta$ -D-glucofuranose are seen only in Traces A and B and are absent in Traces C and D, although glucose is present in ratios Glu:Ile = 1.45:1 (Trace C) and Glu:Ile = 0.36:1 (Trace D). On the other hand, 3,6-(2-methylpropyl)-2,5-diketopiperazine and 2-methyl-1-butanamine (Ret. time 19.34 min) are present only in Traces E and D, although isoleucine is present in the mixture generating Traces B and C. The compounds missing from the pyrolysate of one parent molecule in the mixture, when they were expected to be present, indicates that they react with a compound generated from the other parent molecule. Some new compounds are formed following these reactions, or some reactions taking place in the pure compound are hindered by the presence of the other components.

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## CHAPTER 3

*Physicochemical Aspects of the Pyrolytic Process***3.1. THERMODYNAMIC FACTORS IN PYROLYTIC REACTIONS****General aspects**

The thermal properties of chemical compounds are of obvious interest in pyrolysis studies. These properties can be described using thermodynamic functions [1–3]. One such basic function is the Gibbs free enthalpy or free enthalpy ( $G$ ), which is expressed as follows [2]:

$$G = H - TS = E + pV - TS \quad (3.1.1)$$

where  $H$  is enthalpy (in Joules (J) when measured in SI units) and represents the sum of the system energy  $E$  and  $pV$  ( $p$  = pressure and  $V$  = volume),  $T$  absolute temperature (measured in Kelvin,  $0\text{ K} = -273.15^\circ\text{C}$ ), and  $S$  entropy (in J/deg when measured in SI units).

The variation in the free enthalpy accompanying chemical reactions is obtained from the difference in the sum of standard free enthalpies of the products and the sum of standard free enthalpies of reactants (where standard values noted are considered at 1 atm):

$$\Delta G^\circ = \sum \Delta G^\circ_{\text{products}} - \sum \Delta G^\circ_{\text{reactants}} \quad (3.1.2)$$

Similar equations apply for the enthalpy and the entropy of a system, with expressions given below:

$$\Delta H^\circ = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{reactants}} \quad (3.1.3)$$

$$\Delta S^\circ = \sum \Delta S^\circ_{\text{products}} - \sum \Delta S^\circ_{\text{reactants}} \quad (3.1.4)$$

The values  $\Delta H^\circ$  are the standard *enthalpies of formation* of a given compound and represent the thermal effect of formation of one mole of that compound from elements. The value  $\Delta H^\circ$  also is known as (molar) enthalpy of formation or *heat of formation*, the attribute “standard” being added when the value is given for 1 atm. A zero enthalpy is assigned to each element in its most stable form at standard conditions ( $25^\circ\text{C}$  and 1 atm). For many chemical compounds the values for  $\Delta H^\circ$  and  $\Delta S^\circ$  are known [4–14].

The standard (molar) entropy is the entropy content of one mole of substance at standard temperature and pressure. Unlike standard enthalpies of formation, the  $\Delta S^\circ$  for elements have nonzero values. According to the third law of thermodynamics, only at 0 K is the entropy of an element 0 J/deg/mol. The sum of the incremental values of  $Q_{\text{rev}}/T$  (where  $Q_{\text{rev}}$  is the amount of heat exchanged by the system if the process is reversible) when a mole of substance at 0 K is warmed by its surroundings to 298 K constitute each element’s or compound’s standard molar entropy.

The expression for  $\Delta G^\circ$  contains an enthalpy term and an entropy term and can be obtained using the following formula:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3.1.5)$$

Because  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  are temperature dependent, they must be specified at a certain temperature. The standard values for the thermodynamic functions are typically provided for 298.15 K

(25 °C). However, pyrolysis reactions take place at much higher temperatures. A more rigorous treatment should apply the following corrections:

$$\Delta H^\circ_T = \Delta H^\circ_{298} + \Delta C^\circ_p (T - 298.15) \quad (3.1.6)$$

$$\Delta S^\circ_T = \Delta S^\circ_{298} + \Delta C^\circ_p \ln\left(\frac{T}{298.15}\right) \quad (3.1.7)$$

where  $\Delta C^\circ_p$  = average variation in the *heat capacity* (heat capacity is the measure of the heat required to increase the temperature of a substance by a certain temperature interval).

$\Delta C^\circ_p$  is given by the following equation:

$$\Delta C^\circ_p = \frac{\Delta C^\circ_{p,T} + \Delta C^\circ_{p,298}}{2} \quad (3.1.8)$$

The heat capacities at different temperatures for a chemical reaction are given by the expression:

$$\Delta C^\circ_{p,T} = \sum \Delta C^\circ_{p,T} \text{ products} - \sum \Delta C^\circ_{p,T} \text{ reactants} \quad (3.1.9)$$

This correction is difficult to apply, and practically it is not able to resolve the problem of temperature dependence on  $\Delta H^\circ$  and  $\Delta S^\circ$ . However,  $\Delta C^\circ_p$  is typically small, and its effects on  $\Delta H^\circ$  and  $\Delta S^\circ$  tend to compensate each other when the values for the free enthalpy  $\Delta G^\circ$  are calculated. For this reason, in many examples of estimations of  $\Delta G^\circ$  values at elevated temperatures, the values for 298.15 K are still used. The index for temperature in  $\Delta H^\circ$  and  $\Delta S^\circ$  can be omitted either for  $T = 298.15$  K or for generic discussions about these functions.

An example showing the variation with temperature for  $\Delta H^\circ_T$  and  $\Delta S^\circ_T$  for *n*-butyric acid is shown in Figures 3.1.1 and 3.1.2, respectively. The values were obtained using an estimation method based on a semiempirical molecular orbital calculation performed with the computational package MOPAC-7 [15] with AM1 type parameters.

The free enthalpy  $\Delta G^\circ_T$  can be calculated from  $\Delta H^\circ_T$  and  $\Delta S^\circ_T$  for *n*-butyric acid using equation 3.1.5. For the illustration of the variation of  $\Delta G^\circ_T$  with temperature, the function was calculated based on  $\Delta H^\circ_T$  and  $\Delta S^\circ_T$  at different temperatures, and also based on  $\Delta H^\circ_{298}$  and  $\Delta S^\circ_{298}$  (at 25 °C) when only the explicit value of  $T$  in equation 3.1.5 was varied. The results are shown in Figure 3.1.3.

As seen from Figure 3.1.3, in a range of about 200° of temperature (°C or K), the values for  $\Delta G^\circ_T$  calculated based on  $\Delta H^\circ_{298}$  and  $\Delta S^\circ_{298}$  do not differ too much from the calculation that takes into account the variation with temperature of  $\Delta H^\circ$  and  $\Delta S^\circ$ . However, in a wider range of values, the effect of temperature on  $\Delta G^\circ$  becomes more significant because of the changes in  $\Delta H^\circ$  and  $\Delta S^\circ$  as the temperature increases.

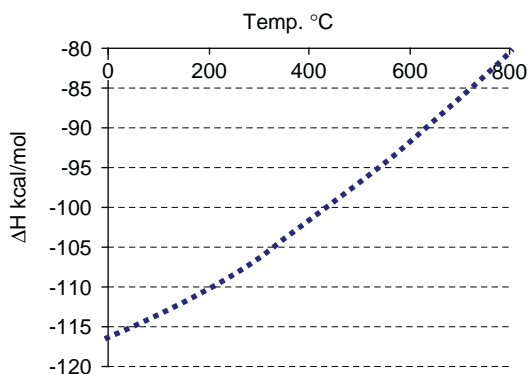


FIGURE 3.1.1. Variation of  $\Delta H^\circ_T$  (kcal/mol) with temperature for *n*-butyric acid.

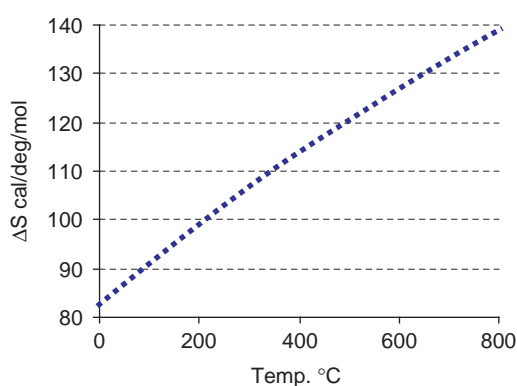


FIGURE 3.1.2. Variation of  $\Delta S^\circ_T$  (cal/deg/mol) with temperature for *n*-butyric acid.

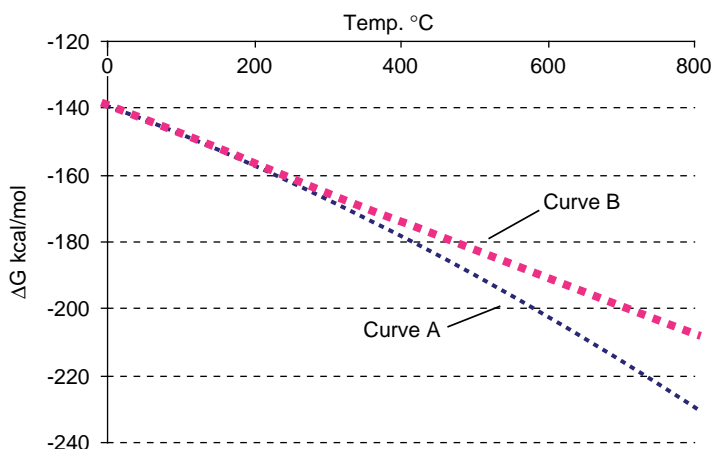


FIGURE 3.1.3. Variation of  $\Delta G^\circ_T$  (kcal/mol) with temperature for *n*-butyric acid calculated by two procedures. Curve A was obtained using equation 3.1.5 with  $\Delta H^\circ_T$  and  $\Delta S^\circ_T$  modified for various temperatures in addition to the explicit value for  $T$ . Curve B was obtained using equation 3.1.5 and  $\Delta H^\circ_{298}$  and  $\Delta S^\circ_{298}$ , changing only the explicit value for  $T$ .

The free enthalpy  $\Delta G^\circ$  of a chemical process is related to the equilibrium constant  $K_p$  of that process. Considering a reaction of the type (in gas phase):



the equilibrium constant  $K_p$  will follow the equation (see rel. 3.2.7):

$$K_p = \frac{p_B^b p_C^c p_D^d}{p_A^a} \quad (3.1.11)$$

where  $p_A$  is partial pressure of component A,  $p_B$  partial pressure of component B,  $p_C$  partial pressure of component C,  $p_D$  partial pressure of component D, etc.

In principle, if  $K_p$  and the initial partial pressure of A are known, it is possible to calculate the yield of the resulting compounds B, C, D, and so on. In thermodynamics, it can be demonstrated [3] that  $K_p$  is

related to the variation of the standard free enthalpy  $\Delta G^\circ$  by:

$$\Delta G^\circ_T = -R T \ln K_p \quad (3.1.12)$$

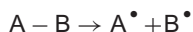
where  $R$  is gas constant (in SI units  $R = 8.31451 \text{ J/deg/mol} = 1.987 \text{ cal/deg/mol}$ ).

Since  $\Delta G^\circ_T$  is temperature dependent,  $K_p$  is also temperature dependent.

### **Bond dissociation energy from thermochemical data**

Evaluation of *bond dissociation energy* is a typical application of thermochemical information related to the prediction of pyrolysis mechanism and indirectly of pyrolysis outcome. As discussed in Section 2.2, a common mechanism found to operate in pyrolytic reactions is elimination involving free radicals. For this reaction, the initiation starts with a pyrolytic cleavage. The bond that will break first is likely to be the one that is the weakest link in the chain. Although the fragmentation in pyrolysis does not take place only at the weaker bond, the weaker ones typically have higher probability of breaking. The information on bond dissociation energy may indicate which bond is more likely to break in a molecule and can be used to estimate the temperature range where the process occurs.

Bond energy is defined as the energy required to separate an isolated molecule (i.e., in gas phase), after the cleavage of a bond, into two fragments (atoms or radicals) at infinite distance. The reaction of bond dissociation can be written as follows:



In practice, instead of bond energy  $\Delta E$  the value of bond enthalpy  $\Delta H$  is measured. The standard enthalpy of a bond is the enthalpy required to break the bond (usually at  $25^\circ\text{C}$  and 1 atm). Assuming the initial molecule and its fragments to be perfect gases, based on rel. 3.1.1 and using the perfect gases law  $pV = nRT$ , the differences between enthalpy and energy can be written as follows:

$$\Delta H - \Delta E = \sum (pV)_{\text{fragments}} - (pV)_{\text{molecule}} = (\Delta n)RT \quad (3.1.13)$$

where  $\Delta n$  is the variation in the number of moles during fragmentation.

The variation in the number of moles with the formation of two fragments is  $n = 1$ , and for  $298^\circ\text{C}$ ,  $\Delta H^\circ - \Delta E^\circ = 2.4789 \text{ kJ/mol} = 0.592 \text{ kcal/mol}$ . True bond energy should be taken at 0 K and not at 298.3 K, which also introduces a small difference between bond energy and bond enthalpy. However, these differences are very small compared to the value of the bond dissociation energy, and, in general, the bond dissociation energy is taken as equal to the negative value for the enthalpy (heat) of formation of the bond  $\Delta H^\circ_f(A-B)$ . This value is considered a direct measure of the bond strength. (It should be noted that since no work is performed in this process, the variation in enthalpy  $\Delta H$  is equal to the variation in heat  $\Delta Q$ ). Based on rel. 3.1.3, the enthalpy of bond dissociation is given by the expression:

$$\Delta H^\circ_f(A-B) = \Delta H^\circ_f(A^\bullet) + \Delta H^\circ_f(B^\bullet) - \Delta H^\circ_f(AB) \quad (3.1.14)$$

Several average bond energies (enthalpies evaluated at  $25^\circ\text{C}$ ) for different bond types are given in Table 3.1.1.

In addition to the nature of the atoms forming the bond, the bond strength depends on the rest of the molecule. The values from Table 3.1.1 give only an estimate for a specific bond strength. More precise bond dissociation energies can be given when the nearest neighbors of the dissociating bond are specified. Table 3.1.2 gives the estimated bond energies in kcal/mol at 298.15 K when the molecular moiety is considered for the bond strength.

Even considering the next neighbor, it is not always possible to obtain a good estimation of the dissociation energy, and additional corrections must be made. For example, when the dissociating bond is in conjugation with a  $\pi$  electron system, the dissociation energy must be decreased with about 16 kcal/mol for a phenyl ring and with about 10 kcal/mol for a double bond. Also, the number of carbons

TABLE 3.1.1. Average bond energies (enthalpies at 298.15 K) in kcal/mol

Single bonds	$\Delta H_f^\circ$ (kcal/mol)	Single bonds	$\Delta H_f^\circ$ (kcal/mol)	Multiple bonds	$\Delta H_f^\circ$ (kcal/mol)
H–H	104.2	B–F	150	C=C	146
C–C	83	B–O	125	N=N	109
N–N	38.4	C–N	73	O=O	119
O–O	35	N–CO	86	C=N	147
F–F	36.6	C–O	85.5	C=O (CO <sub>2</sub> )	192
Si–Si	52	O–CO	110	C=O (aldehyde)	177
P–P	50	C–S	65	C=O (ketone)	178
S–S	54	C–F	116	C=O (ester)	179
Cl–Cl	58	C–Cl	81	C=O (amide)	179
Br–Br	46	C–Br	68	C=O (halide)	177
I–I	36	C–I	51	C=S (CS <sub>2</sub> )	138
H–C	99	C–B	90	N=O (HONO)	143
H–N	93	C–Si	76	P=O (POCl <sub>3</sub> )	110
H–O	111	C–P	70	P=S (PSCl <sub>3</sub> )	70
H–F	135	N–O	55	S=O (SO <sub>2</sub> )	128
H–Cl	103	S–O	87	S=O (DMSO)	93
H–Br	87.5	Si–F	135	P=P	84
H–I	71	Si–Cl	90	P≡P	117
H–B	90	Si–O	110	CO	258
H–S	81	P–Cl	79	C≡C	210
H–Si	75	P–Br	65	N≡N	226
H–P	77	P–O	90	C≡N	213

in an aliphatic radical R, as indicated in Table 3.1.2, plays a considerable role in the value of bond dissociation. The higher the number of carbon atoms in R, the lower is the dissociation energy. Extensive information on bond dissociation energies can be found in the literature [14].

The values for  $\Delta H^\circ$  (A–B) indicated in Table 3.1.2 lead to some observations regarding bond stability. For example, for the strength of a C–H bond, the increase in the  $\pi$  character of the adjacent bond leads to an increase in the C–H bond strength. In Table 3.1.2, the following values can be noticed: 133 kcal/mol for (CH<sub>3</sub>)<sub>3</sub>C–H, 111.1 kcal/mol for (Ph)<sub>3</sub>C–H, 109 kcal/mol for (CH<sub>2</sub>=CH)<sub>2</sub>–H, and 101.0 kcal/mol for (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>–H. Similar observations show decrease in the strength for the series (CH<sub>3</sub>)<sub>3</sub>C–H > (CH<sub>3</sub>)<sub>2</sub>CH–H > (CH<sub>3</sub>)CH<sub>2</sub>–H > ((CH<sub>3</sub>)<sub>2</sub>CH)<sub>2</sub>–H > ((CH<sub>3</sub>)<sub>3</sub>C)<sub>2</sub>–H and also for the series (PhCH<sub>2</sub>)<sub>2</sub>–H > (PhCHR)<sub>2</sub>–H > (PhCR<sub>2</sub>)<sub>2</sub>–H. The effect on the second carbon is opposite. The bond strength decreases in the series: (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>–H > (PhCH<sub>2</sub>)<sub>2</sub>–H > (CH<sub>2</sub>=CHCH<sub>2</sub>)<sub>2</sub>–H > (Ph<sub>2</sub>CH)<sub>2</sub>–H. For bonds between two carbon atoms, similar tendencies can be noticed by inspection of Table 3.1.2. For the bonds to heteroatoms, the strength increases with the increase in the atomic number in the order (CH<sub>3</sub>)<sub>3</sub>C–H < (NH<sub>2</sub>)<sub>3</sub>–H < (HO)<sub>3</sub>–H < (F)<sub>3</sub>–H. The trend is maintained when one of the hydrogens on the main atom is replaced with alkyl groups.

When the enthalpy for the homolytic dissociation of the bond A–B is not known, it can be derived [5] from tabulated heats of formations  $\Delta H_f^\circ$  of the AB compound and from that of free radicals A<sup>•</sup> and B<sup>•</sup> using rel. 3.1.14. The values for  $\Delta H_f^\circ$  (AB) are available for many compounds [3,6–12], and some values for small molecules are given in Table 3.1.3 [12].

Tables with heats of formation for radicals also are available in literature (e.g., [13]). Some enthalpies of formation and some entropies for a number of common free radicals are given in Table 3.1.4.

A simple example for the calculation of the bond energy between a hydrogen atom and the carbon in ethane (C<sub>2</sub>H<sub>5</sub>–H) would lead to the following calculation:  $\Delta H_f^\circ$  (H<sup>•</sup>) = 52.1 kcal/mol,  $\Delta H_f^\circ$  (C<sub>2</sub>H<sub>5</sub><sup>•</sup>) = 29.0 kcal/mol,  $\Delta H_f^\circ$  (C<sub>2</sub>H<sub>6</sub>) = –20.03 kcal/mol, and the resulting bond energy is  $\Delta H_f^\circ$  (C<sub>2</sub>H<sub>5</sub>–H) = 52.1 + 29.0 – (–20.03) = 101.13 kcal/mol, in very good agreement with the value from Table 3.1.2 of 101.0 kcal/mol.

TABLE 3.1.2. Bond dissociation energies at 298.15 K in kcal/mol considering the nearest neighbor in different molecular moieties [3]

Group-	-Group (Energy, kcal/mol)								
	-H	-F	-Cl	-Br	-I	-CH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> R	-CHR <sub>2</sub>
H-	104.2								
F-	136.4	38.0							
Cl-	103.2	60.0	57.1						
Br-	87.5	56.2	52.1	45.4					
I-	70.7	52.1	49.7	43.0	35.6				
CH <sub>3</sub> -	104.2	108.3	84.1	70.0	56.2	88.2			
C <sub>2</sub> H <sub>5</sub> -	101.0	106.0	81.0	69.1	53.1	84.5	81.6		
R-CH <sub>2</sub> -	98.2	106.1	81.0	69.1	53.1	85.1	81.4	80.5	
(CH <sub>3</sub> ) <sub>2</sub> CH-	98.5								
R <sub>2</sub> CH-	94.2	105.2	81.0	67.6	53.1	83.2	80.2	78.2	76.0
(CH <sub>3</sub> ) <sub>3</sub> C-	96.5								
R <sub>3</sub> C-	91.1	102.1	79.1	63.1	50.2	80.1	76.9	75.0	73.1
CH <sub>2</sub> =CHCH <sub>2</sub> -	88.0								
Ph-	111.1	125.2	100.1	80.1	65.0	94.0	90.6	91.1	83.2
Ph-CH <sub>2</sub> -	88.5	90.1	68.1	51.1	40.2	72.2	76.0	62.1	55.0
Ph(CH <sub>3</sub> )CH-	86.0								
Ph(CH <sub>3</sub> ) <sub>2</sub> C-	84.0								
Ph <sub>2</sub> CH-	79–82								
1,3-cyclohexadiene	76.0								
CH <sub>2</sub> =CH-	109.0		86.0		55.0	90.1	90.0	90.1	85.1
Allyl-	86.8					73.6	70.3	70.3	67.7
CH≡C-	133.0					100.1		109.2	103.2
CH(O)CH <sub>2</sub> -	92–95								
CF <sub>3</sub> -	106.1	129.3	85.1	70.0	54.0	100.1			
FCH <sub>2</sub> -	101.0								
CCl <sub>3</sub> -	96.1	106.1	73.1	54.0					
ClCH <sub>2</sub> -	100.0								
HO-	119.3					91.1		91.1	92.0
CH <sub>3</sub> O-	103.0								
RO-	102.1	59.0	49.0			80.1		80.1	81.0
PhO-	87.0						67.0		
HOCH <sub>2</sub> -	96.0								
HO(CH <sub>3</sub> )CH-	94.0								
CH <sub>3</sub> OCH <sub>2</sub> -	93–94.5								
CH(O)-	87.2					75.0		71.0	
CH <sub>3</sub> C(O)-	89.0								
RC(O)-	86.0		82.2	67.2	51.1	82.2		77.2	
HOC(O)CH <sub>2</sub> -	94–97.5								
HOC(O)-	92.5								
HC(O)O-	105.0								
CH <sub>3</sub> C(O)O-	104–106								
RC(O)O-	112.1								
CH <sub>3</sub> OC(O)CH <sub>2</sub> -	93–98								
CH <sub>3</sub> OC(O)-	92.5								
NH <sub>2</sub> -	106.0					79.1		78.2	77.2

TABLE 3.1.2. *cont'd*

Group-	-Group (Energy, kcal/mol)								
	-H	-F	-Cl	-Br	-I	-CH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>2</sub> R	-CHR <sub>2</sub>
H <sub>2</sub> NCH <sub>2</sub> -	93.5								
CH <sub>3</sub> NH-	99.0								
RNH-	92.0								
PhNH-	85–93						70–77		
(CH <sub>3</sub> ) <sub>2</sub> N-	91.5								
HC(O)O-	105.0								
CH <sub>3</sub> C(O)O-	104–106								
RC(O)O-	112.1								
CH <sub>3</sub> OC(O)CH <sub>2</sub> -	93–98								
CH <sub>3</sub> OC(O)-	92.5								
NH <sub>2</sub> -	106.0					79.1		78.2	77.2
H <sub>2</sub> NCH <sub>2</sub> -	93.5								
CH <sub>3</sub> NH-	99.0								
RNH-	92.0								
PhNH-	85–93						70–77		
(CH <sub>3</sub> ) <sub>2</sub> N-	91.5								
R <sub>2</sub> N-	86.0								
CN-						110.2			
SH-	90.1								
RS-	88.2		65.0						
R <sub>3</sub> C-	70.0								
Ph-	78.2	115.0							
Ph-CH <sub>2</sub> -		77.2	56.01						
CH <sub>2</sub> =CH-	81.0	101.1	70.0	112.1					
Allyl-			58.0	78.4					
CH≡C-		119.3			110.2				
CF <sub>3</sub> -						97.0			
CCl <sub>3</sub> -							87.2		
HO-	91.1	112.1	77.2					51.1	
RO-	78.2	101.1							33.9
CH(O)-		90.1	50.2						
RC(O)-			63.1					44.0	
C(O)O-			55.0						
NH <sub>2</sub> -	77.2	100.1	65.0						
CN-		130.3	95.1	121.2					
CH(O)-	60.0								
RC(O)-	60.0	60.0							
RC(O)O-	59.0		30.1						
NH <sub>2</sub> -	90.1	98.2							
RNH-				37.0					
R <sub>2</sub> N-					42.1				
CN-						145.3			
SH-							30.1		
RS-								63.1	

Note: R indicates aliphatic substituent.

TABLE 3.1.3. *Enthalpies of formation kcal/mol and entropies cal/T/mol for several small molecules in ideal gas form at 298.15 K*

Small molecule	Molecule name	$\Delta H_f^\circ$ (kcal/mol)	$\Delta S^\circ$ (cal/T/mol)
H <sub>2</sub>	Hydrogen	0.0	31.23
N <sub>2</sub>	Nitrogen	0.0	45.79
O <sub>2</sub>	Oxygen	0.0	49.03
O <sub>3</sub>	Ozone	33.89	57.20
NO	Nitrous oxide	21.38	50.37
NO <sub>2</sub>	Nitrogen dioxide	7.91	57.34
SO <sub>2</sub>	Sulfur dioxide	-70.95	59.32
SO <sub>3</sub>	Sulfur trioxide	-94.59	61.37
CO <sub>2</sub>	Carbon dioxide	-94.05	51.10
CO	Carbon monoxide	-26.42	47.24
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide	-32.47	55.63
(CN) <sub>2</sub>	Dicyan	73.86	57.73
CHCl <sub>3</sub>	Chloroform	-24.70	70.66
CH <sub>2</sub> Cl <sub>2</sub>	Methylenechloride	-22.79	64.61
C <sub>2</sub> F <sub>4</sub>	Tetrafluoroethylene	-223.03	62.48
CH <sub>4</sub>	Methane	-17.83	44.51
C <sub>2</sub> H <sub>2</sub>	Ethyne (acetylene)	54.54	47.98
C <sub>2</sub> H <sub>4</sub>	Ethene (ethylene)	12.55	52.47
C <sub>2</sub> H <sub>6</sub>	Ethane	-20.03	54.87
C <sub>3</sub> H <sub>6</sub>	Propene	4.78	63.84
C <sub>3</sub> H <sub>8</sub>	Propane	-25.02	64.53
C <sub>4</sub> H <sub>6</sub>	1, 3-Butadiene	26.48	68.58
C <sub>4</sub> H <sub>10</sub>	<i>n</i> -Butane	-30.06	74.06
C <sub>4</sub> H <sub>10</sub>	2-Methylpropane	-32.26	70.62
C <sub>5</sub> H <sub>8</sub>	Isoprene	18.10	75.44
C <sub>6</sub> H <sub>6</sub>	Benzene	19.81	64.36
C <sub>6</sub> H <sub>5</sub> -CH <sub>3</sub>	Toluene	11.99	76.65
C <sub>10</sub> H <sub>8</sub>	Naphthalene	35.99	79.65
<i>p</i> -C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	<i>p</i> -Xylene	4.30	84.32
C <sub>6</sub> H <sub>5</sub> -CH=CH <sub>2</sub>	Styrene	35.44	82.51
CH <sub>2</sub> =CH-CN	Acrylonitrile	43.98	62.93
HF	Hydrofluoric acid	-65.14	41.53
HCl	Hydrochloric acid	-22.06	44.67
HBr	Hydrobromic acid	-8.71	47.49
HI	Hydroiodic acid	6.33	49.37
HCN	Hydrocyanic acid	32.30	48.21
H <sub>2</sub> O	Water	-57.80	45.11
H <sub>2</sub> C=O	Formaldehyde	-25.95	52.31
CH <sub>3</sub> OH	Methanol	-48.02	57.31
HCOOH	Formic acid	-90.48	59.44
C <sub>2</sub> H <sub>5</sub> OH	Ethanol	-56.15	67.06
CH <sub>3</sub> -CHO	Acetaldehyde	-39.72	63.08
CH <sub>3</sub> OCH <sub>3</sub>	Dimethylether	-43.99	63.90
H <sub>2</sub> C=CO	Ketene	-11.40	57.80



TABLE 3.1.3. *cont'd*

Small molecule	Molecule name	$\Delta H_f^\circ$ (kcal/mol)	$\Delta S^\circ$ (cal/T/mol)
C <sub>2</sub> H <sub>4</sub> O	Oxirane	-12.58	58.05
NH <sub>3</sub>	Ammonia	-11.0	46.03
H <sub>2</sub> S	Hydrogen sulfide	-4.9	49.17
CH <sub>3</sub> -COOH	Acetic acid	-103.31	67.52
CH <sub>3</sub> COCH <sub>3</sub>	Acetone	-51.34	70.66
CH <sub>3</sub> CH(OH)CH <sub>3</sub>	Isopropyl alcohol	-65.17	73.91
C <sub>6</sub> H <sub>5</sub> OH	Phenol	-20.04	73.34
C <sub>4</sub> H <sub>4</sub> O	Furan	-8.29	63.87
C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	Pyrazine	46.80	67.01
C <sub>5</sub> H <sub>5</sub> N	Pyridine	33.54	67.58
NaCl	Sodium chloride	-43.36	54.91
NaCl (solid)	Sodium chloride	-98.26	

### The estimation of free enthalpy

Although extensive databases for the values of various thermodynamic functions are available (see, e.g., [16]), the measured values for larger molecules are not known in many cases. Because of the utility of these values, estimation of enthalpy and entropy from structural characteristics of the compounds has been the subject of a significant number of studies [3], and several procedures can be used for obtaining estimates.

One set of procedures for obtaining such values is based on quantum chemical methods. These include *ab initio* calculations performed with computational packages such as Gaussian 94 [17] or later versions of this package [18], semiempirical molecular orbital calculations performed with computational packages such as MOPAC-7 [15,19,20], and calculations based on the electron density functions performed with computational packages such as BLYP/DZVP [21–23]. These procedures provide good estimates of various thermodynamic parameters (mainly for small molecules and usually in ideal gas form).

Another set of procedures used to estimate free enthalpies is based on the assumption that the values for  $\Delta H$  and  $\Delta S$  can be obtained from additive fragment contributions with some corrections due to two center contributions or other structural factors [4,23]. This type of procedure (additivity model) can use, for example, estimation formulas of the form:

$$\Delta H^\circ = \sum \Delta H^\circ_{\text{fragment}} + \sum \Delta H^\circ_{\text{structure}} \quad (3.1.15)$$

$$\Delta S^\circ = \sum \Delta S^\circ_{\text{fragment}} + \sum \Delta S^\circ_{\text{structure}} \quad (3.1.16)$$

Individual values for the heat of formation  $\Delta H^\circ$  of fragments in various molecular moieties are available [4]. A simplified set of parameters for both heats of formation ( $\Delta H^\circ$ ) and for entropies ( $\Delta S^\circ$ ) of several common fragments in organic molecules and for some structural factors are given in Tables 3.1.5 and 3.1.6, respectively. The resulting values are assumed to give estimations for the compounds in ideal gas form [24]. More elaborate methods for the calculation of heats of formation using fragments and contribution from structure are available in literature [4,24,25].

Values from Tables 3.1.5 and 3.1.6 can be used in calculations. For example, the enthalpy for acetic acid phenyl ester obtained from fragments is  $\Delta H^\circ = \Delta H^\circ_{\text{CH}_3} + \Delta H^\circ_{\text{COO-}} + \Delta H^\circ_{\text{-C}_6\text{H}_5} = 69.75$  kcal/mol as compared to the experimental 66.85 kcal/mol. The entropy calculated from fragments is 90.34 cal/deg/mol as compared to the experimental 94.77 cal/deg/mol. For the free radicals, some group contributions are given in Table 3.1.7.

The estimation of the free enthalpy of formation using the data from Tables 3.1.5 to 3.1.7 leads to values for the gaseous state of the molecule (in some instances hypothetical state). However, not all

TABLE 3.1.4. Enthalpies of formation kcal/mol and entropies in cal/T/mol at 298.15 K for some common free radicals [13]

Radical	Name	$\Delta H_f^\circ$ (kcal/mol)	$\Delta S^\circ$ (A°) (cal/T/mol)
H•	Hydrogen radical	52.1	27.41
F•	Fluorine radical	19.1	37.94
Cl•	Chlorine radical	28.9	39.48
Br•	Bromine radical	26.8	41.82
I•	Iodine radical	25.6	43.21
OH•	Hydroxyl radical	8.9	43.91
O:	Oxygen atom	59.6	38.5
CH•••	Methyldiyne	142.4	
CH <sub>2</sub> ••	Methylene	92.3	
CH <sub>3</sub> •	Methyl	35.0	46.4
CH <sub>2</sub> =CH•	Vinyl	69	
HC≡C•	Ethynyl	135	
CH <sub>3</sub> -CH••	Methylmethylene	90.3	
CH <sub>3</sub> -CH <sub>2</sub> •	Ethyl	29.0	43.9
(CH <sub>3</sub> ) <sub>2</sub> CH•	Isopropyl	21.5	
CH <sub>2</sub> =CH-CH <sub>2</sub> •	Allyl	41.0	59.3
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> •	Propyl	21.0	
CH <sub>3</sub> -CH•-CH <sub>3</sub>	2-Propyl	16.8	
CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>2</sub> -CH <sub>2</sub> •	Butyl	16.0	
C <sub>2</sub> H <sub>5</sub> -CH•-CH <sub>3</sub>	2-Butyl	12.0	
(CH <sub>3</sub> ) <sub>2</sub> -CH-CH <sub>2</sub> •	<i>i</i> -Butyl	13.0	
(CH <sub>3</sub> ) <sub>3</sub> -C•	<i>tert</i> -Butyl	12.5	
C <sub>6</sub> H <sub>5</sub> •	Phenyl	81.2	68.4
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> •	Benzyl	48.5	
C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )CH•		41.0	
C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> C•		33.0	
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH•		66.5	
C <sub>6</sub> H <sub>7</sub> •		50.0	
CH <sub>3</sub> O•		5.0	56.0
CH <sub>3</sub> -CO•	Methylcarbonyl	-5.0	
CH <sub>3</sub> -CO-CH <sub>2</sub> •	Propanonyl	-8.0	73.4
CHO•	Formyl radical	10.5	53.6
HOCH <sub>2</sub> •		-4.0	58.4
CH <sub>3</sub> OCH <sub>2</sub> •		-3.0	
HO(CH <sub>3</sub> )CH•		-14.5	
O <sub>2</sub> (singlet)	Oxygen excited	22.56	48.25
CH••-OH	Hydroxymethylene	27.2	
CH <sub>3</sub> O•	Methoxy	5.0	56.0
CH <sub>3</sub> CO•		-3	
C <sub>2</sub> H <sub>5</sub> O•	Ethoxy	-3.2	66.3
C <sub>6</sub> H <sub>5</sub> O•	Phenoxy	12.0	
HO(O)C•	HOOC radical	50.0	
HC(O)O•	Formate radical	-38.0	
CH <sub>3</sub> COO•	Acetate radical	-49.5	

TABLE 3.1.4. *cont'd*

Radical	Name	$\Delta H_f^\circ$ (kcal/mol)	$\Delta S^\circ$ (A <sup>*</sup> ) (cal/T/mol)
HC(O)CH <sub>2</sub> <sup>*</sup>		0.0	
HOC(O)CH <sub>2</sub> <sup>*</sup>		-61.5	
CH <sub>3</sub> C(O)OCH <sub>2</sub> <sup>*</sup>		-55.0	
NH <sub>2</sub> <sup>*</sup>		44.0	
H <sub>2</sub> NCH <sub>2</sub> <sup>*</sup>		36.0	
CN <sup>*</sup>	Cyanide	104.0	48.4
CH <sub>3</sub> -NH <sup>*</sup>	CH <sub>3</sub> -NH radical	41.5	
(CH <sub>3</sub> ) <sub>2</sub> N <sup>*</sup>		34.5	
C <sub>6</sub> H <sub>5</sub> -NH <sup>*</sup>		58.0	
CF <sup>***</sup>	Fluoromethylidyne	61.0	
C(O)F <sup>*</sup>	COF radical	-42.3	
CHO <sup>*</sup>	HCOF radical	-90.0	
FCH <sub>2</sub> <sup>*</sup>		-7.0	
ClCH <sub>2</sub> <sup>*</sup>		28.0	
CF <sub>2</sub> <sup>**</sup>	Difluoromethylene	-45.0	
CF <sub>3</sub> <sup>*</sup>	Trifluoromethyl	-112.4	
CF <sub>3</sub> -CH <sub>2</sub> <sup>*</sup>	CF <sub>3</sub> -CH <sub>2</sub> radical	-123.6	
CCl <sup>***</sup>	Chloromethylidyne	111.3	
CHCl <sup>**</sup>	Chloromethylene	80.0	
C <sub>6</sub> H <sub>5</sub> O <sup>*</sup>	Phenoxy	12.9	74.5
COCl <sup>*</sup>	COCl radical	-15.0	
CCl <sub>2</sub> <sup>**</sup>	Dichloromethylene	55.0	
CCl <sub>3</sub> <sup>*</sup>	Trichloromethyl	17.0	
CBr <sub>3</sub> <sup>*</sup>	Tribromomethyl	64.7	
Cl <sub>3</sub> <sup>*</sup>	Triiodomethyl	117.3	
C <sub>6</sub> H <sub>4</sub> Cl <sup>*</sup> ( <i>ortho</i> )	Chlorophenyl	72.4	78.8

compounds are in gas phase. For this reason, corrections must be made to the gaseous state of a compound in order to estimate the free enthalpy for a specific reaction involving compounds in liquid or solid (crystalline or amorphous) state. A number of empirical rules are available for the change from gas phase to a condensed phase, and a selection of such corrections is given in Table 3.1.8 [26].

Another procedure for the calculation of free enthalpy, based in part on the additivity properties of the values for  $\Delta H^\circ$  and  $\Delta S^\circ$ , uses correlation equations for a series of homolog compounds or compounds containing a repetitive unit. Since the compounds in a homolog series differ by the same fragment, it can be expected that the values in a series are linear. This relationship is exemplified by the variation of the heat of formation of the normal series of aliphatic carboxylic acids in Figure 3.1.4.

Figure 3.1.4 shows, indeed, linearity for the acids (between acetic and eicosanoic) for both condensed phase and gaseous phase. For example, the values for  $\Delta H^\circ$  for condensed phase can be obtained as a function of the number of carbons ( $n$ ) in the molecule using the equation:

$$\Delta H^\circ = -7.17n - 101.04 \text{ kcal/mol} \quad (3.1.17)$$

The results from Figure 3.1.4 also show that for aliphatic saturated acids the difference in  $\Delta H^\circ$  between gas phase and condensed phase is not a constant and varies with the number of carbons in the molecule, with an average that is larger than that indicated in Table 3.1.8. Association of carboxylic acids through hydrogen bonds in condensed phase is probably the reason for this difference. The results from an estimation using a semiempirical molecular orbital calculation (MOPAC-7 with AM1 type parameters) are situated between the gas and the condensed form results.

TABLE 3.1.5. Contribution of molecular fragments to heats of formation and entropies (generated in ideal gas at 298.15 K [24])

Fragment	$\Delta H_{\text{fragment}}^{\circ}$ (kcal/mol)	$\Delta S_{\text{fragment}}^{\circ}$ (cal/deg/mol)
-CH <sub>3</sub>	-10.01	22.71
-CH <sub>2</sub> -	-5.00	24.38
>CH-	-2.03	28.68
>C<	-0.12	33.46
=CH <sub>2</sub>	6.29	7.17
=CH-	8.51	9.08
=C<	9.70	11.95
=C=	32.74	-4.78
≡CH	27.17	-7.77
≡C-	26.94	-5.98
>C <sub>ar</sub> H	2.99	6.21
>C <sub>ar</sub> -	5.98	9.08
>C <sub>ar</sub> ⋯	5.02	5.14
-p-phenylene-	23.9	43.02
-phenyl	20.8	39.91
-F	-46.61	-1.43
-Cl	-9.56	-2.15
-Br	-1.53	-3.35
-I	13.53	-9.80
-CN	25.41	-6.81
-OH	-38.14	11.95
-O-	-23.90	16.73
-HC=O	-29.68	6.21
>C=O	-31.91	9.56
-COOH	-93.93	28.20
-COO-	-80.54	27.72
-NH <sub>2</sub>	4.52	24.50
-NH-	15.61	28.68
>N-	24.40	35.85
>N <sub>ar</sub>	16.49	11.95
-SH	4.54	7.89
-S-	11.09	-5.74
>S	14.34	-14.34
-S-S-	10.99	-6.69
-SO <sub>2</sub> -	-69.14	36.33
>S=O	-16.11	15.06
-NO <sub>2</sub>	-7.72	34.18
-ONO	-5.02	31.07
-ONO <sub>2</sub>	-21.03	50.91
-NC	49.09	40.8
-NO	18.09	32.4

TABLE 3.1.6. Contributions from the combination of two structural factors or from special structure characteristics to the heat of formation and entropy of molecules in ideal gas at 298.15 K [3,24]

Structural factors		$\Delta H_{\text{structure}}^{\circ}$ (kcal/mol)	$\Delta S_{\text{structure}}^{\circ}$ (cal/deg/mol)
-CH <sub>2</sub> -	=C<	0.31	
-CH <sub>2</sub> -	-CN	0.95	
>CH-	=C<	0.57	
>CH-	-CN	1.12	
>C<	>C<	3.17	
>C<	=C<	1.86	
>C<	-CN	2.08	
=CH-	=CH-	-1.65	
=CH-	=C<	-1.36	
=CH-	-CN	1.48	
3-Atom ring		23.90	-29.16
4-Atom ring		23.90	-26.29
5-Atom ring		4.78	-23.90
6-Atom ring		-0.72	-16.73
Conjugated double bonds		-4.30	3.82
cis-trans conversion		-1.43	1.67

TABLE 3.1.7. Contribution of radicals to heat of formation and entropies (in ideal gas form at 298.15 K [24])

Radical	Name	$\Delta H_f^{\circ}(\text{A}\cdot)$ (kcal/mol)	$\Delta S^{\circ}(\text{A}\cdot)$ (cal/deg/mol)
-CH <sub>2</sub> •	Alkyl	33.9	-1.0
≡C•	Alkyl	38.0	15.1
-O•	Alkoxy radical	8.0	-1.9
-C•(O)		5.0	-10.0
-C(O)O•		-2.6	10.0
-C(O)NH•		4.1	10.0
-O-O•	Peroxy	7.5	0.0

TABLE 3.1.8. Average corrections to the heats of formation and entropies for changes from gas phase to condensed phase

Phase of reagents	Phase of products	$\Delta H^{\circ}$ (kcal/mol) correction	$\Delta S^{\circ}$ (cal/deg/mol) correction
Gas	Solid amorphous	-1.67	3.59
Gas	Solid crystalline	-4.06	9.56
Liquid	Solid amorphous	0.00	-9.56
Liquid	Solid crystalline	1.91	-7.17
Solid crystalline	Solid crystalline	0.00	-9.56

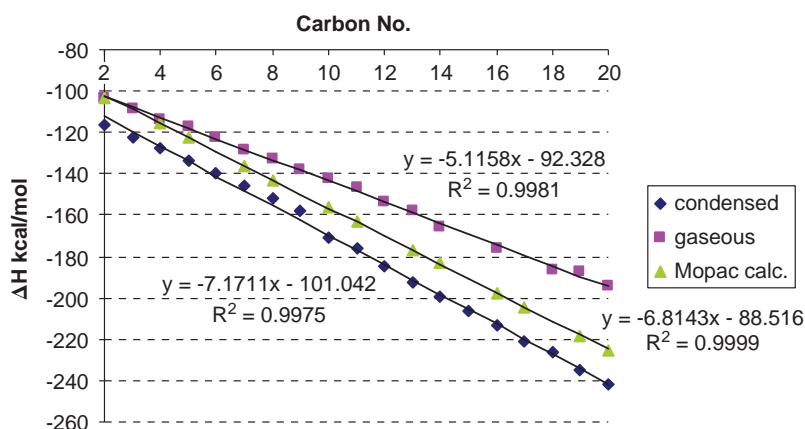


FIGURE 3.1.4. Variation of the heat of formation  $\Delta H^\circ$  (kcal/mol) with the number of carbon atoms in the molecule for normal monocarboxylic acids in condensed phase (experimental), gaseous phase (experimental), and calculated using MOPAC-7 semiempirical molecular orbital package with AM1 type parameters.

Similar expressions for the values of  $\Delta H^\circ$  can be generated for other homologous compound series. For saturated hydrocarbons (gas state), the expression has the form:

$$\Delta H^\circ = -4.90n - 10.97 \text{ kcal/mol} \quad (3.1.18)$$

For 1-alkenes, the expression of  $\Delta H^\circ$  for the homologous series is given by the expression:

$$\Delta H^\circ = -5.016n + 20.564 \text{ kcal/mol} \quad (3.1.19)$$

Similar linearity is obtained for the values of entropy in a homologous series of compounds. Figure 3.1.5 shows the variation of entropy for the normal series of aliphatic carboxylic acids (calculated using MOPAC-7 package).

As shown in Figure 3.1.5, the values for  $\Delta S^\circ$  for the carboxylic acids are a linear function of the number  $n$  of carbons in the molecule and have the expression:

$$\Delta S^\circ = 8.01n + 54.59 \text{ cal/deg/mol} \quad (3.1.20)$$

As previously shown, the data used for generating the correlation equations can be either experimental or calculated values of a thermodynamic parameter. Some other examples for this type of evaluation can be found in the literature [3]. For example, for saturated linear hydrocarbons the expression for  $\Delta S^\circ$  as a function of the number of carbon atoms in the molecule is the following:

$$\Delta S^\circ = 9.47n + 31.79 \text{ cal/deg/mol} \quad (3.1.21)$$

The use of thermodynamic information, either experimental or obtained from estimations can provide useful guidance regarding the explanation or even prediction of the outcome of pyrolytic processes.

### The estimation of bond energy

Bond energies represent an important parameter in pyrolytic reactions that involve free radicals. For this reason some effort was made to obtain bond dissociation energies by procedures other than direct measurements. The values can be obtained from the values of free enthalpies of the initial molecule and its fragments using rel. 3.1.14, and if these enthalpies are estimated, it can be concluded that the bond energies (enthalpies) also represent estimated values (see, e.g., [27–30]). However, other procedures can be utilized for the purpose of the estimation of bond dissociation energy. Among these procedures are those based on fitting a Morse potential [31,32], based on infrared (IR) stretching frequencies data

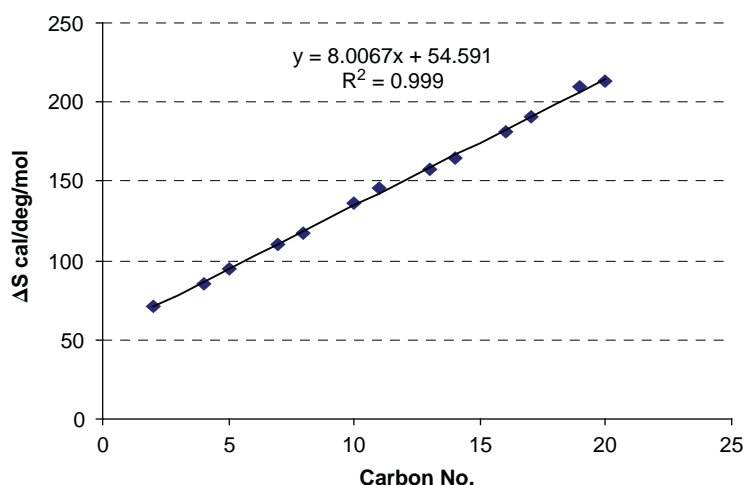


FIGURE 3.1.5. Variation of the entropy  $\Delta S^\circ$  (cal/deg/mol) with the number of carbon atoms in the molecule for normal aliphatic monocarboxylic acids calculated using MOPAC-7 semiempirical molecular orbital package with AM1 type parameters.

[33], using kinetic reaction rate values [34], based on ionization potentials of radicals [35], or using empirical correlations between a specific molecular property and the distance between the atoms in the molecule [36]. Direct evaluation of bond energies is also possible based on the electron population analysis (electron density between atoms) [37–42].

### The application of thermodynamic information to pyrolytic reactions

The course of a pyrolytic reaction may be determined kinetically or thermodynamically. When the reaction is able to reach equilibrium, thermodynamic factors control the reaction outcome. The calculation of a free enthalpy for a chemical reaction allows the prediction of the reaction course, and the reactions are displaced toward the formation of products when  $\Delta G^\circ_T < 0$ . Considering rel. 3.1.5 and 3.1.2 for  $\Delta G^\circ_T$ , it can be noticed that the increase in temperature will favor reactions resulting in an increase in entropy  $\Delta S^\circ$  of the system (since it appears as  $-T \Delta S^\circ$  in the expression of  $\Delta G^\circ_T$ ). For this reason, decomposition reactions, which generate several fragments from one parent molecule and have a positive value for  $\Delta S^\circ$ , typically are favored by the temperature increase. On the other hand, condensation reactions (such as Diels–Alder condensations), which generate one product from two reagents and have a negative value for  $\Delta S^\circ$  of the reaction, are not favored by the temperature increase.

The calculation of the temperature for which  $\Delta G^\circ_T = 0$  allows the determination of the specific temperature at which a reaction is favored thermodynamically. For pyrolytic reactions, the temperature  $T$  satisfying the condition  $\Delta G^\circ_T = 0$  is defined as the *ceiling temperature*  $T_c$ . From equation 3.1.5 the expression for  $T_c$  becomes:

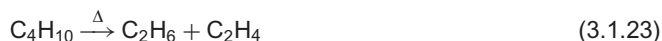
$$T_c = \frac{\Delta H^\circ_T}{\Delta S^\circ_T} (\text{K}) \quad (3.1.22)$$

where  $\Delta H^\circ_T$  and  $\Delta S^\circ_T$  are given by equations 3.1.3 and 3.1.4, respectively.

The ceiling temperature  $T_c$  can be considered the temperature at which a pyrolytic process will reach equilibrium. It may be seen, therefore, as a recommended temperature for pyrolysis. However, in practice, the application of the above relation for solid samples is not straightforward. The theory was developed for ideal systems (sometimes in gas phase), and, although in principle this theory should hold true for any system, its application to condensed phases may be accompanied by effects difficult to account for (phase change, melting, cage effect [3] etc.). The reaction rate also could be low at calculated  $T_c$  values. For this reason, temperatures 50 °C or 100 °C higher than  $T_c$  frequently must be used as practical values of the temperature in the pyrolysis of a specific compound.

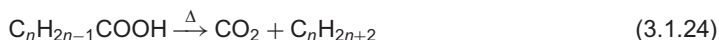
Although the utility of ceiling temperature is limited for practical purposes, the evaluation of the free enthalpy of reaction for pyrolytic processes provides important guidance regarding the potential reaction path. Several examples of the utility of thermodynamic calculations are given below.

Pyrolysis of butane is one such example. The reaction can be written as follows:



For this reaction,  $\Delta H^\circ_{298} = 22.5 \text{ kcal/mol}$  and  $\Delta H^\circ_{1000} = 21.5 \text{ kcal/mol}$ . Positive values for  $\Delta H^\circ$  indicate endothermic reactions. The entropy of the reaction is favorable since the formation of two molecules from one ( $\Delta n = 1$ ) leads to an increase in entropy. The values for the reaction entropy (calculated using rel. 3.1.4) are  $\Delta S^\circ_{298} = 33.2 \text{ cal/mol/deg}$  and  $\Delta S^\circ_{1000} = 31.5 \text{ cal/mol/deg}$ . Using rel. 3.1.5 at ambient temperature (298.15 K), the value for the free enthalpy is  $\Delta G^\circ_{298} = 12.6 \text{ kcal/mol}$ , and at 1000 K  $\Delta G^\circ_{1000} = -10.0 \text{ kcal/mol}$ . At ambient temperature the value for the equilibrium constant becomes  $K_p = 5.74 \times 10^{-10} \text{ atm}$ , and therefore, a very low conversion of butane takes place at equilibrium. At 1000 K (or 827 °C) the constant becomes  $K_p = 153.3 \text{ atm}$ , indicating a high yield of conversion at equilibrium.

The decomposition of aliphatic monocarboxylic acids is another example where the thermodynamic factors allow an estimation of their thermal decomposition temperature in the reaction:



The expression for  $\Delta G^\circ_T$  for this reaction can be obtained using rel. 3.1.2, and  $\Delta H^\circ_T$  and  $\Delta S^\circ_T$  values for the acids are generated by rel. 3.1.15 and 3.1.17, respectively. The values for  $\Delta H^\circ_T$  and  $\Delta S^\circ_T$  for the hydrocarbons are generated by rel. 3.1.16 and 3.1.18, respectively, and the values for  $\Delta H^\circ_T$  and  $\Delta S^\circ_T$  for  $\text{CO}_2$  can be obtained from Table 3.1.1. All these values combined lead to:

$$\Delta G^\circ_T = 2.27(n-1) + 3.19 - (T + 273.15) \frac{1.46(n-1) + 20.29}{1000} \quad (3.1.25)$$

where  $T$  is expressed in °C and  $n$  number of carbons in the molecule of the acid.

For the condition  $\Delta G^\circ_T = 0$ , the resulting  $T_c$  as a function of the number of carbon atoms in the molecule of the acid is as follows:

$$T_c(^{\circ}\text{C}) = \frac{[(2.27(n-1) + 3.19)1000]}{1.46(n-1) + 20.29} - 273.15 \quad (3.1.26)$$

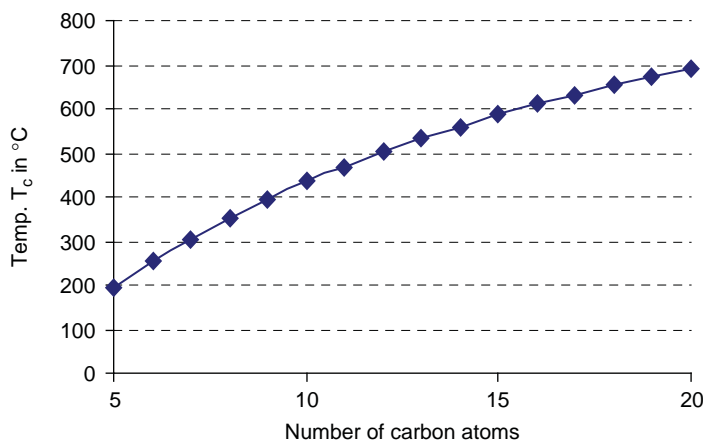


FIGURE 3.1.6. Variation of the  $T_c$  values as a function of the number of carbon atoms in aliphatic carboxylic acids.



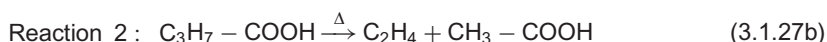
TABLE 3.1.9. The values for  $\Delta H^\circ$  in kcal/mol and  $\Delta S^\circ$  in cal/deg/mol of each compound participant in reactions 3.1.27(a–c) (the values for butyric acid are taken with opposite sign), followed by the resulting  $\Delta G_T^\circ$  for the corresponding reactions

	Butyric acid	CO <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	Reaction 1	C <sub>2</sub> H <sub>4</sub>	Acetic acid	Reaction 2	H <sub>2</sub> O	2-Butenal	Reaction 3
$\Delta H^\circ$	129.72	–94.05	–25.67	10.00	12.55	–116.06	26.21	–57.80	–26.56	45.36
$\Delta S^\circ$	–86.63	51.10	60.20	24.67	52.47	67.52	33.36	45.11	88.18	46.66

The variation of  $T_c$  as a function of the number of carbons in the aliphatic carboxylic acid is shown in Figure 3.1.6.

As seen from Figure 3.1.6, the stability to heat regarding the decarboxylation reaction seems to increase with the increase in the length of the aliphatic chain of the carboxylic acid. However, the results are sensitive to small variations in the values of the parameters used for the calculations, and the correct  $\Delta H^\circ_T$  and  $\Delta S^\circ_T$  for different temperatures are seldom available. For example, the results shown in Figure 3.1.6 do not agree with the known fact that the carboxylic acids with a low number of carbon atoms are quite stable at temperatures up to 200 °C.

Thermodynamic information also can be used for estimating which reaction path is more likely in a pyrolytic reaction when more alternatives are possible. As an example, pyrolysis of butyric acid can follow one of the following decomposition paths:



The values for  $\Delta H^\circ_T$  and  $\Delta S^\circ_T$  contributing to the values of  $\Delta G^\circ_T$  of each participant in these reactions are shown in Table 3.1.9.

The values from Table 3.1.9 were used for the calculation of  $\Delta G^\circ$  (applying rel. 3.1.5) at different temperatures and are plotted in Figure 3.1.7.

It can be seen from Figure 3.1.7 that reaction 1 is thermodynamically possible at temperatures as low as 200 °C, reaction 2 can begin only above 500 °C, and reaction 3 can begin only above 700 °C. Among the three reactions, the most likely to occur is reaction 1.

In summary, thermodynamic information is useful in pyrolysis. However, it is not always sufficient for determining the course of a reaction, such as when the reaction cannot reach equilibrium because the reaction is too slow and the values of the kinetic factors are determinant [43].

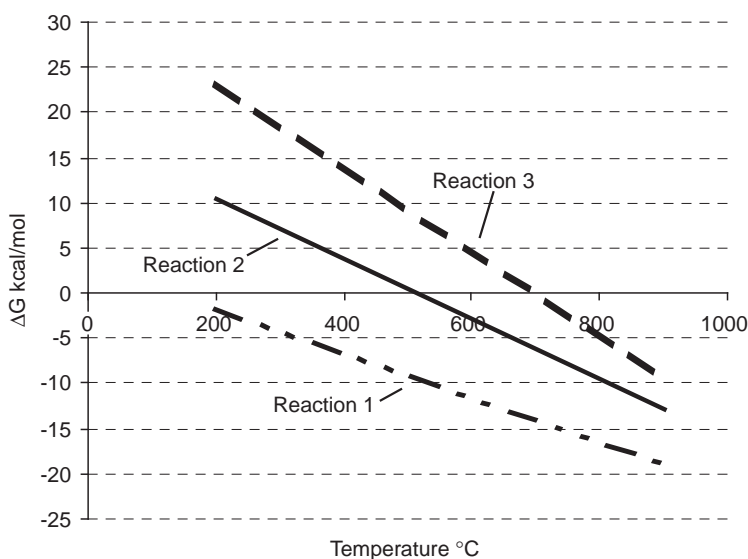


FIGURE 3.1.7. Variation of  $\Delta G^\circ$  in kcal/mol for reactions 3.1.27a, 3.1.27b, and 3.1.27c as a function of temperature.

### 3.2. KINETIC FACTORS IN PYROLYTIC REACTIONS

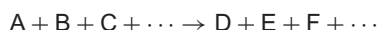
#### General aspects

The *reaction rate* of a chemical process where A is a reactant and B is a product is defined as the variation of the concentration of A or of B vs. time. The reaction rate can be expressed using the following relation:

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} \quad (3.2.1)$$

where [A] and [B] = (molar) concentrations at time  $t$  during the reaction (measured in mol/L).

Since pyrolysis reactions are complex, the reaction is not always a simple transformation of compound A into compound B. If in a chemical reaction of the type:



the rate of reaction depends linearly on the concentration of reactant A, then the reaction is still of the first order and the reaction rate has the expression:

$$-\frac{d[A]}{dt} = k[A] \quad (3.2.2)$$

where  $k$  is rate constant ( $k$  units being  $s^{-1}$ ).

This type of reaction follows *first order* kinetics. The rate constant,  $k$ , is temperature dependent and it is a constant only in isothermal conditions. In pyrolysis, because of the reactions taking place after the first decomposition step, the overall kinetics of the reaction may be different from first order.

It is possible that the rate of a reaction depends on the concentrations of the A and B reactant species simultaneously. In this case the dependence is given by the expression:

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B] \quad (3.2.3)$$

where  $k$  is rate constant ( $k$  units being  $L \text{ mole}^{-1} s^{-1}$ ).

This type of reaction follows *second order* kinetics. Note that the rate constant  $k$ , in this case, has different units from those of the rate constant for the first order kinetics.

Some chemical reactions have a reaction rate of the form:

$$-\frac{d[A]}{dt} = k[A]^n \quad (3.2.4)$$

where  $n$  is reaction order.

The value of  $n$  can be an integer, or for certain chemical reactions, it can be a fraction.

Similar to numerous thermodynamic data, information on the kinetics of many reactions is available in the literature. One such example is the NIST database [44]. Many data are published in the dedicated journal, *Journal of Physical and Chemical Reference Data*.

#### Arrhenius equation

In order to understand how the constant  $k$  depends on temperature and the thermodynamic parameters of the system, it can be assumed that the chemical reactions can take place only when the molecules collide. Following this collision, an intermediate state called an activated complex is formed. The difference in the energy of the isolated reactants and the energy of the activated complex, which is the maximum energy that the system passes through to form the products, is indicated as the activation energy  $\Delta E^\ddagger$  (the symbol  $\Delta$  for the difference is frequently neglected). For a reaction with no intermediates, the energy profile along the reaction coordinate is shown in Figure 3.2.1. The reaction

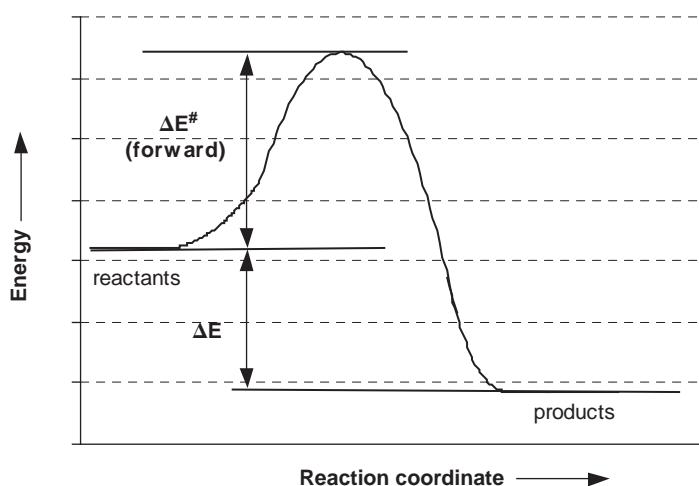


FIGURE 3.2.1. Variation of energy along the reaction coordinate for a simple system.

coordinate is a parameter related to the progress of the reaction and is not usually specified, but it may represent the distance between the centers of the two reacting molecules, the distance between two atoms that are going to separate or to connect, etc. The reaction rate will depend on the difference between the energy of the reactants and the energy of the activated complex (the activation energy  $E^\ddagger$  also can be indicated as  $E^a$ ).

The reaction rate will also depend on the frequency of collisions. Based on these assumptions, it can be shown that  $k$  has the following expression (Arrhenius reaction rate equation):

$$k = A \exp\left(-\frac{E^\ddagger}{RT}\right) \quad (3.2.5)$$

where  $A$  is *frequency factor* (parameter related to the frequency of collisions). Expressed in logarithm form, the equation can be written as  $\log_{10} k = \log_{10}(A) + 0.4343 \cdot (E^\ddagger/R) \cdot (1/T)$ , which is an equation of the first degree in  $(1/T)$ . A plot of this equation ( $\log_{10} k$  as a function of  $1/T$ ) is known as an Arrhenius plot. The plot of  $\log_{10} k$  (or  $\ln_e k$ ) as a function of  $1/T$  for a chemical reaction is used to determine the frequency factor and the activation energy for single rate-limited thermally activated processes when the plot is a straight line.

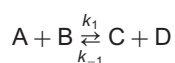
Equation 3.2.5 indicates the explicit dependence of the rate constant  $k$  on temperature (in K). However, both  $A$  and  $E^\ddagger$  are not strictly temperature independent, and some variation with temperature of these parameters can be expected [45]. For this reason, sometimes a modified Arrhenius equation is used. This equation has the form:

$$k = BT^n \exp\left(-\frac{E^\ddagger}{RT}\right) \quad (3.2.6)$$

where  $B$  is temperature independent frequency factor and  $n$  a constant.

Equations 3.2.5 and 3.2.6 indicate that the reaction rate  $k$  increases with the increase in temperature. For this reason, many chemical reactions that are thermodynamically possible but have very low values for  $k$  and virtually do not take place at room temperature occur at elevated temperature.

The parameters  $A$  and  $E^\ddagger$  from Arrhenius equation 3.2.5 can be related to the equilibrium constant  $K$  of a chemical process. Considering a simple reversible reaction of the form:



the equilibrium is characterized by a forward rate constant  $k_1$  and a reverse rate constant  $k_{-1}$ . Based on the law of chemical equilibrium (Guldberg and Waage), these rate constants are related to the

equilibrium constant  $K$  by the expression:

$$K = \frac{[C][D]}{[A][B]} = \frac{k_1}{k_{-1}} \quad (3.2.7)$$

(The molar concentrations  $[A]$ ,  $[B]$ , ... are related to the partial pressures  $p_A$ ,  $p_B$ , ... if the components are gases by the expression:  $p_A = (RT)[A]$ , ...)

From rel. 3.1.12 for the expression of equilibrium constant and from Arrhenius equation given by rel. 3.2.5 for the two kinetic constants  $k_1$  and  $k_{-1}$ , the following relations between the kinetic and thermodynamic parameters can be obtained:

$$\Delta H^\circ = E^\#_{\text{forward}} - E^\#_{\text{reverse}} + (\Delta n) RT \quad (3.2.8)$$

$$\Delta S^\circ = R \ln \left( \frac{A_{\text{forward}}}{A_{\text{reverse}}} \right) + (\Delta n) R [1 + \ln (R^* T)] \quad (3.2.9)$$

where  $E^\#_{\text{forward}} - E^\#_{\text{reverse}} = \Delta E$ , the difference in energy between the reactants and the products as shown in Figure 3.2.1.

The  $\Delta n$  term accounts for the change in the number of moles in the stoichiometric equation for the reaction. This term is necessary because the thermochemical quantities are tabulated for a standard state at 1 atm, while the rate constants are expressed in concentration units. Because of this convention two constants are necessary,  $R = 1.987 \text{ kcal/mol}$  and  $R^* = 0.082 \text{ L/mol/deg}$ .

Rel. 3.2.8 and 3.2.9 can be written so as to separate the variables necessary in the calculation of kinetic constants. This will lead to:

$$E^\#_{\text{forward}} - E^\#_{\text{reverse}} = \Delta H^\circ - (\Delta n) RT \quad (3.2.10)$$

$$\ln \left( \frac{A_{\text{forward}}}{A_{\text{reverse}}} \right) = \frac{\Delta S^\circ}{R} - (\Delta n) [1 + \ln (R^* T)] \quad (3.2.11)$$

These relations do not provide independent values for the activation energy  $E^\#$  and for the frequency factor  $A$  since the parameters are connected by Arrhenius equation, which can be written in the form:

$$\log(k) = \log A - \frac{E^\#}{2.303RT} \quad (3.2.12)$$

(where the notation  $\log$  is used for  $\log_{10}$  while  $\ln$  has been used for  $\log_e$ ). However, values for  $\Delta H^\circ$  and  $\Delta S^\circ$  are frequently available in literature, and some direct results can be obtained for either the forward reaction or for the reverse reaction. In these cases, the calculation of the third parameter is possible, and some kinetic values can be calculated from thermodynamic ones.

### **Kinetic factors in pyrolytic reactions**

Assuming that a specific chemical reaction is thermodynamically favorable, the rate of the reaction is the factor determining the reaction course. For pyrolytic reactions, the variation of the molar concentration  $[A]$  of a substance during pyrolysis is not the most appropriate parameter to be monitored. The calculation of  $[A]$  can be a problem for many types of samples, and very frequently during pyrolysis more than one decomposition process takes place. In this case, the overall reaction kinetics must be considered.

A more convenient parameter for monitoring pyrolytic reactions is the sample weight. Since most pyrolysis products are volatile at pyrolysis temperatures, the reaction can be monitored based on the sample weight loss. For a reaction of the first order, by multiplying expression 3.2.2 on both sides with the volume  $V$  and the molecular weight  $M$  of the substance  $A$ , the following

expression is obtained:

$$-\frac{dW}{dt} = kW \quad (3.2.13)$$

where  $W$  is weight (mass) of the sample any time during the reaction and  $W = [A]VM$ .

This type of equation can approximate (with good results) the kinetics for many pyrolytic processes. Equation 3.2.13 can be integrated to give:

$$\ln W|_{t=0}^t = -kt \quad \text{or} \quad \ln \frac{W}{W_0} = -kt \quad \text{or} \quad \frac{W}{W_0} = \exp(-kt) \quad (3.2.14)$$

where  $W_0$  is the initial sample weight (at  $t = 0$ ).

In some cases, the pyrolysis leaves a residue, for example, of char of the weight  $W_f$  (final weight). In this case rel. 3.2.13 becomes:

$$-\frac{dW}{dt} = k(W - W_f) \quad (3.2.15)$$

This type of expression can be applied to pyrolytic processes even if the reaction is not of first order, when the reaction rate is described by the following relation:

$$-\frac{dW}{dt} = k(W - W_f)^n \quad (3.2.16)$$

The reaction order  $n$  is not necessarily an integer. Relations of the type 3.2.13, 3.2.14, or 3.2.15, which were used for weight, can be applied for other parameters that can be measured for pyrolytic processes. Examples of such parameters are the residual mass fraction ( $W/W_0$ ) and the volatilized mass fraction  $\alpha = 1 - W/W_0$  (also known as conversion). The conversion is equal to the ratio of the volatilized mass to the initial mass.

When the pyrolytic process does not occur in gas phase, different problems appear regarding the application of the previous formulas. Although equations of the type 3.2.13 can be used in certain cases, these may lead to incorrect results. Various empirical models were developed for describing the reaction kinetics during the pyrolysis of solid samples [46]. Most of these models attempt to establish equations that will globally describe the kinetics of the process and fit the pyrolysis data.

The temperature dependence of the rate of reactions is particularly important for the pyrolytic processes. Equations 3.2.5 and 3.2.13 can be combined leading to the expression:

$$-\frac{dW}{dt} = A \exp\left(-\frac{E^\#}{RT}\right) W \quad (3.2.17)$$

This equation can be used for understanding the choice of certain pyrolysis parameters, such as heating rate and maximum temperature required for heating. This temperature can be different from the ceiling temperature calculated from thermodynamic data. With known values for the frequency factor  $A$ , activation energy  $E^\#$ , and temperature  $T$ , equation 3.2.17 can be integrated to provide the value of weight loss at a certain temperature. The integrated form of equation 3.2.17 leads to the following expression for the residual mole fraction  $W/W_0$ :

$$\frac{W}{W_0} = \exp\left(-A \exp\left(-\frac{E^\#}{RT}\right) t\right) \quad (3.2.18)$$

In a case in which the reaction generates a residue  $W_f$ , equation 3.2.18 should be modified as follows:

$$\frac{(W - W_f)}{(W_0 - W_f)} = \exp\left(-A \exp\left(-\frac{E^\#}{RT}\right) t\right) \quad (3.2.19)$$

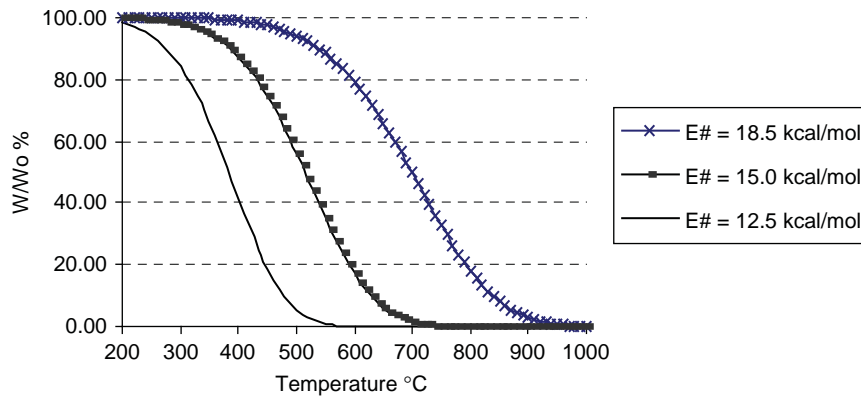


FIGURE 3.2.2. Variation with temperature of  $WW_0$  % for three different substances having  $E^\# = 18.5$  kcal/mol,  $E^\# = 15.0$  kcal/mol, and  $E^\# = 12.5$  kcal/mol,  $A = 1000 \text{ s}^{-1}$ . Pyrolysis is done for 10 s in a hypothetical flash mode that brings the substance instantaneously to the specified temperature.

Equation 3.2.18 or 3.2.19 can be used to demonstrate how the kinetic factor influences the weight loss in a hypothetical case involving the pyrolysis of a substance that is instantaneously exposed to a specific temperature for a given time interval. For exemplification, the variation of the residual mole fraction  $WW_0$  % during such pyrolysis is shown in Figure 3.2.2 for three different substances, which have  $E^\# = 18.5$  kcal/mol,  $E^\# = 15.0$  kcal/mol, and  $E^\# = 12.5$  kcal/mol, respectively, and a value for  $A = 1000 \text{ s}^{-1}$  when heating time of 10 s is used.

As seen from Figure 3.2.2, for the reaction with high activation energy ( $E^\# = 18.5$  kcal/mol), the decrease in weight starts only around 550 °C. Below this temperature the weight loss (and therefore, the decomposition) is practically absent. Lower activation energy values show that the decrease in weight occurs not only at lower temperatures, but also only after reaching a specific value. A simple transformation of equation 3.2.18 or 3.2.19 allows one to obtain a likely temperature where the sample loses 99% of its initial weight. The expression for this temperature, which can be indicated as kinetically required  $T_k$  (in K), is the following:

$$T_k = \frac{E^\#}{R[\ln(tA) - 1.527]} \quad (3.2.20)$$

The values for the activation energies frequency factors are not well known for many reactions. However, they can be obtained from thermogravimetric (TG) studies. Using the notations  $T_f$  and  $T_i$  for the final and initial temperature in a thermogram,  $T_s$  for the temperature of inflection in the TG curve (typically obtained from the derivative curve DTG), and  $\omega$  for the fraction of material degraded at temperature  $T$  ( $\omega$  is equal to the volatilized mass fraction  $\alpha$  when all decomposed material generates gases), the activation energy for the major step in a thermogram can be determined, for example, from the expression [47]:

$$\ln[-\ln(1-\omega)] = \left(\frac{E^\#}{RT_i^2}\right) \left(\frac{100}{T_f - T_i}\right) (T - T_s) + C \quad (3.2.21)$$

where  $C$  is a constant that can be obtained from the plot of  $\ln[-\ln(1-\omega)]$  vs.  $(T - T_s)$ .

The frequency factor  $A$  can be calculated using the expression [2]:

$$A = \frac{\beta E^\# \exp E^\# / RT}{RT_{\max}^2} \quad (3.2.22)$$

where  $\beta$  is heating rate and  $T_{\max}$  is temperature corresponding to the maximum degradation rate ( $T_{\max}$  can be measured from the DTG curve).

Besides the reaction rate  $k$ , which provides a description of how fast a certain process takes place at a given temperature, some "integral" parameters (within a time range) were defined for the same purpose. One such parameter is the half decomposition time  $t_{1/2}$ , which is the time required to get  $W/W_0 = 1/2$ . Making the approximation that  $k$  does not vary with the heating time, the formula for  $t_{1/2}$  calculated from equation 3.2.17 is the following:

$$t_{1/2} = \frac{\log 2}{k} \quad (3.2.23)$$

The required approximations for the validity of equation 3.2.23 are rather difficult to meet in practice.

### Kinetics of gas phase pyrolytic reactions

In the pyrolysis of pure compounds, a single reagent molecule is transformed into one or more products. In condensed phase, the pyrolysis process is typically complicated, sometimes involving the reaction between two molecules of the same species. However, in gas phase, the initial step of pyrolysis can be truly a unimolecular reaction (see, e.g., [48]). In order for a molecule A to undergo a fragmentation of the type:



it is necessary that the molecule achieves a sufficient level of energy. In gas phase, this energy is generated by inelastic collisions either with other A molecules or with an inert molecule M (Lindemann theory). Labeling as M either the same (as A) or a different (inert) molecule, the collision process can be described as follows:



where  $A^*$  designates the molecule with sufficient energy to dissociate,  $k_1$  is the reaction rate constant for the reaction, and  $k_2$  the reaction rate of the de-excitation process.

Some of the  $A^*$  molecules will react generating the products as shown below:



For gas components, the partial pressures  $p_A$ ,  $p_B$ , ... can be related to molar concentrations by the expression:  $p_A = (RT)[A]$ ,  $p_B = (RT)[B]$ , ..., and the variation in the concentration of B can be described by the equation:

$$\frac{d[B]}{dt} = -\frac{d[A]}{dt} = k_3[A^*] \quad (3.2.27)$$

On the other hand, the change in the concentration of  $A^*$  is described by the equation:

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_2[A^*][M] - k_3[A^*] \quad (3.2.28)$$

In stationary state conditions the concentration of  $[A^*]$  does not change,  $d[A^*]/dt = 0$  and:

$$[A^*] = \frac{k_1[A][M]}{k_2[M] + k_3} \quad (3.2.29)$$

Expression 3.2.29 can be introduced in equation 3.2.27 to give:

$$\frac{d[A]}{dt} = -\frac{k_1 k_3 [M]}{k_2 [M] + k_3} [A] \quad (3.2.30)$$



From expression 3.2.30 an “effective unimolecular rate coefficient”  $k_{\text{uni}}$  can be defined by the formula:

$$k_{\text{uni}} = \frac{k_1 k_3 [M]}{k_2 [M] + k_3} \quad (3.2.31a)$$

This effective rate coefficient  $k_{\text{uni}}$  is dependent on the concentration (pressure) of the participating gases (except for some limiting cases), and for a certain interval of values when the concentration (pressure) of M varies, the value of  $k_{\text{uni}}$  will vary. When molecules M are those of the reacting gas,  $[M] = [A]$ . However, in an extreme case, when  $k_2 [M]$  is much higher than  $k_3$  (the deactivation process is much more important than the decomposition),  $k_3$  is neglected in the denominator, and the equation 3.2.30 is reduced to the following expression:

$$\frac{d[A]}{dt} = -\frac{k_1 k_3}{k_2} [A] \quad (3.2.32)$$

The expression 3.2.31a indicates that at a given high pressure of the gas undergoing a unimolecular reaction, the kinetic of the reaction is of the first order (the change in concentration depending linearly on the pressure of the gas). The rate constant in this case is known as the “limiting high pressure rate constant”  $k^\infty$  where:

$$k_{\text{uni}} = k^\infty = \frac{k_1 k_3}{k_2} \quad (3.2.33)$$

The other limiting case is obtained when the value of  $k_2 [M]$  is much smaller than  $k_3$  and the reaction becomes of second order:

$$\frac{d[A]}{dt} = -k_1 [M][A] \quad (3.2.34)$$

The reaction rate  $k_1$  is indicated in this case as a “low pressure” rate constant  $k^\circ$ , and the reaction is of second order. The values of gas pressures where the reaction rate  $k_{\text{uni}}$  becomes  $k^\infty$  are dependent on temperature. An example of expected variation of  $k_{\text{uni}}$  with the gas pressure (at a given temperature) is depicted in Figure 3.2.3. The pressure of gas necessary to reduce the rate constant to one half of its limiting high pressure value  $k^\infty$  is indicated as “falloff pressure”  $P_{1/2}$ , and the region between the high pressure limit and the low-pressure limit is indicated as “falloff region.”

At pressures intermediate to the high- and low-pressure limits (in the falloff region), the rate constant can be estimated by the formula:

$$k_{\text{uni}} = \frac{k^\circ k^\infty [M]}{k^\circ [M] + k^\infty} \quad (3.2.31b)$$

This formula can be modified to generate a more accurate description of the values of  $k_{\text{uni}}$  in the falloff region, by using the “Troe” parameters. With these parameters a factor  $F$  is calculated and is used to multiply expression 3.2.31b to obtain an accurate  $k_{\text{uni}}$ . For this purpose, a “falloff parameter”  $F_{\text{cent}}$  is first calculated using four Troe parameters ( $a$ ,  $b$ ,  $c$ ,  $d$ ) using the expression:

$$F_{\text{cent}} = (1 - a) \exp\left(\frac{-T}{b}\right) + a \exp\left(\frac{-T}{c}\right) + \exp\left(\frac{T}{d}\right) \quad (3.2.35)$$

The expression of the factor  $F$  is given by the formula:

$$-\log F = \frac{1 + [(\log P_r + C)/(N - 0.14(\log P_r + C))]^{+2}}{\log F_{\text{cent}}} \quad (3.2.36)$$

where the reduced pressure  $P_r = k^\circ [M]/k^\infty$ ,  $N = 0.75 - 1.27 \log F_{\text{cent}}$ , and  $C = -0.4 - 0.67 \log F_{\text{cent}}$ .

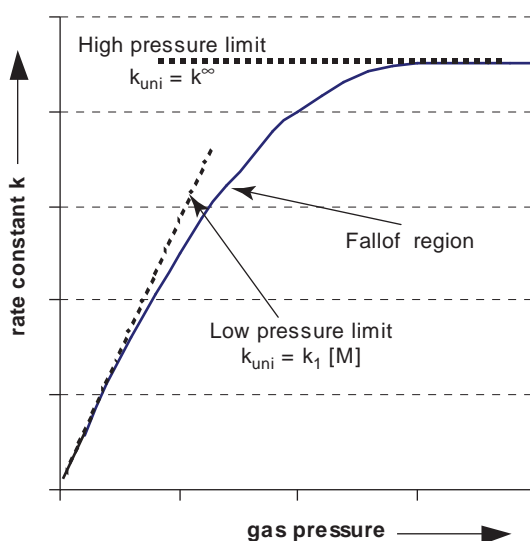


FIGURE 3.2.3. Expected variation of  $k$  with the gas pressure at a fixed temperature in a unimolecular reaction.

The rate constant in unimolecular reactions also can be estimated using Rice–Ramsperger–Kessel–Marcus (RRKM) theory [49]. This theory takes into account the transition state theory of chemical reactions and uses the energies (frequencies) of various normal modes of vibration and rotation in the calculation. The calculation of the rate constant is done following RRKM theory using the expression:

$$k_{\text{RRKM}} = \frac{1}{h} \frac{\sum^*(E - E_0)}{\rho(E)} \quad (3.2.37)$$

where  $E$  is the internal energy of the molecule for which the rate coefficient is estimated,  $E_0$  the critical energy necessary for the molecule to react,  $\sum^*(E - E_0)$  the number of states of the transition state in the range  $E - E_0$ ,  $\rho(E)$  the density of states of the equilibrium geometry at energy  $E$ , and  $h$  Planck's constant.

The study of unimolecular reactions taking place in gas phase received considerable attention mainly because this type of reaction is common in the pyrolysis occurring in important industrial processes. Among these is hydrocarbon pyrolysis taking place in oil processing and in the use of hydrocarbon fuels. However, the pyrolysis reaction in gas phase is not limited to the unimolecular initiation reaction. Other reactions types may be encountered. For hydrocarbons pyrolysis, as an example, some of these reactions are listed below:

- Initiation reaction by a bimolecular process  $\text{RH} + \text{R}'\text{H} \rightarrow \text{R}^\bullet + \text{R}'\text{H}_2^\bullet$
- Hydrogen abstraction  $\text{R}^\bullet + \text{R}'\text{H} \rightarrow \text{R}'^\bullet + \text{RH}$
- Radical decomposition  $\text{R}^\bullet \rightarrow \text{R}'^\bullet + \text{R}''\text{H}$
- Radical addition to unsaturated molecules  $\text{R}^\bullet + \text{R}'\text{H} \rightarrow \text{R}''^\bullet$
- Radical combination  $\text{R}^\bullet + \text{R}'^\bullet \rightarrow \text{R}-\text{R}'$
- Radical disproportionation  $\text{R}^\bullet + \text{R}'^\bullet \rightarrow \text{RH} + \text{R}'\text{H}$
- Concerted reactions  $\text{RH} + \text{R}'\text{H} \rightarrow \text{R}''\text{H} + \text{R}'''\text{H}$
- Retro Diels–Alder reactions (see Section 3.2)
- Radical isomerizations  $\text{R}^\bullet \rightarrow \text{R}'^\bullet$

The evaluation of the parameters in Arrhenius equation governing these types of processes has been performed for many pyrolytic processes (see, e.g., [50]).

The complexity of reactions occurring during pyrolysis/oxidation in gas phase has been studied using computer modeling that allows the calculation of the composition of the resulting gas mixture at specific

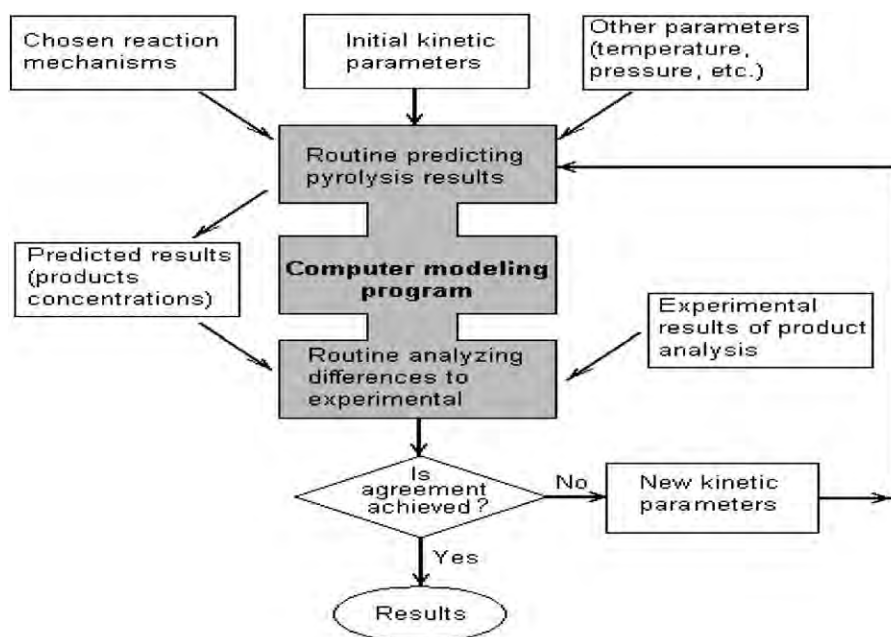


FIGURE 3.2.4. Simplified diagram of a computer program that calculates optimum kinetic parameters to predict pyrolysis yields for gas phase reactions.

initial component ratios, temperatures, pressures, and time along the reaction path [51,52]. The choice of potential reactions and the choice of the thermodynamic and kinetic parameters included in the model lead to a specific result. From the agreement of the predicted result and the experimental information, it is possible to assess the correctness of the model and to obtain optimum values for the kinetic parameters that predict the correct composition of the pyrolysate [51,52]. A number of such programs are described in the literature [53–57]. A simplified diagram of this type of program is shown in Figure 3.2.4. The initial data regarding the kinetic parameters usually are obtained from various experimental studies and may or may not be subject to optimization.

### Models for the kinetics of the pyrolytic processes of solid samples

The kinetics equation of the type described by rel. 3.2.13 is commonly applied for describing the overall reaction kinetics during pyrolysis. However, this equation provides only an approximation for a case in which the process is not composed of a single reaction [58]. The pyrolysis of solid samples is usually a complicated process, and rel. 3.2.13 may lead to erroneous results. The simpler relations valid for the kinetics in homogeneous systems do not fit well the experimental data for solid samples. Factors related to heterogeneous reactions must be taken into account in this case. A series of models have been developed for a better description of the process and can be found in the dedicated literature [59–61].

A more empirical approach [62] for describing the kinetics of the pyrolytic reactions in solid state is to use a parametric equation that includes formulas for all possible categories of kinetics mechanisms known to occur for the chemical reactions of solid samples. Considering the conversion  $\alpha = 1 - W/W_0$ , which is the mass fraction of the reacted substance at the time  $t$ , the empirical kinetics equation for heterogeneous systems can be expressed in the general form:

$$\frac{d\alpha}{dt} = -kf(\alpha) \quad (3.2.38)$$

TABLE 3.2.1.10. Common values from literature [63] for  $m$ ,  $n$ , and  $p$  in equation (3.2.39)

$m$	$n$	$p$	Type of process
0	0	0	Phase boundary controlled reaction
0	1/2, 2/3	0	Phase boundary controlled reaction
0	1	0	Unimolecular decay
$m < 1$ , 3/4	0	0	Random nucleation
1	0	0	Linear growth of nuclei
-1	0	0	Diffusion
0	0	-1	Diffusion
$0.5 < m < 1$	$0.5 < n < 1$	0	Nucleation
$m > 1$	$n < 1$	0	Linear growth of nuclei
0	1	1/2, 2/3, 3/4	Growth of nuclei
0	0	-1	Diffusion
$m$	$n$	$p$	Any complicated case

where  $k$  is rate constant given by Arrhenius equation and  $f(\alpha)$  is a function that can be chosen of the form:

$$f(\alpha) = (1 - \alpha)^n (\alpha)^m [-\ln(1 - \alpha)]^p \quad (3.2.39)$$

The terms in equation 3.2.39 attempt to describe the reaction rate controlled by the movement of the phase boundary, diffusion, nucleation in solid state, etc., and different values (including zero values) for  $m$ ,  $n$ , and  $p$  were proposed in literature [63]. Different combinations of  $m$ ,  $n$ , and  $p$  values were found suitable for describing different dominating processes. Table 3.2.1 indicates some common values for  $m$ ,  $n$ , and  $p$  used in equation 3.2.38. For the reactions in solid state, several other empirical equations as well as numerical methods were proposed to better simulate the reaction rate dependence on temperature [64,65]. Computer programs are utilized also to simulate the rate of pyrolysis for compounds of industrial importance.

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## CHAPTER 4

*Instrumentation Used in Pyrolysis***4.1. OPTIMIZATION OF THE PYROLYTIC PROCESS FOR A SPECIFIC GOAL*****General aspects***

The definition of pyrolysis as a chemical reaction induced by heat alone needs the specification that the process should take place at a temperature significantly higher than ambient. Otherwise, any chemical decomposition caused by thermal energy but taking place at a very low temperature or in a very long period of time would be considered pyrolysis. Even with this restriction, many known chemical processes can be classified as pyrolysis. Some of these pyrolytic processes are unintentional or occur naturally and are typically associated with burning. In other instances, the pyrolytic process is performed intentionally and has a specific purpose.

Very common is the pyrolysis performed to obtain analytical information. One common application of analytical pyrolysis is to use it for the characterization of a material after its chemical degradation induced by thermal energy. The type of analytical information can be qualitative, quantitative, or structural. Pyrolysis itself, being a chemical reaction, does not provide analytical data unless it is associated with some kind of measurement process. The measurement is commonly part of a typical analytical technique such as a chromatographic or spectroscopic one. The purpose of the analytical technique is the analysis of the pyrolysis products (i.e., the pyrolysate). This type of application usually is geared toward polymer analysis or composite material analysis. The analysis of intact polymers is typically difficult. Polymers are not volatile and some of them have low solubility in most solvents. Therefore, the direct application of powerful analytical tools such as gas chromatography/mass spectroscopy (GC/MS) or high performance liquid chromatography (HPLC) cannot be done directly on most polymers. The same is true for many composite materials. Pyrolysis of these kinds of samples (polymers, composite organic materials) generates, in most cases, smaller molecules. These can be analyzed using GC/MS, HPLC, or other sensitive analytical procedures. From the “fingerprint” of the pyrolysis products, valuable information can be obtained about the initial sample. In this way, analytical pyrolysis allows the use of sensitive analytical methods for the analysis of samples, either polymeric or non-polymeric, that are not originally fit for a particular analytical method.

Quantitation using pyrolytic techniques is feasible although less frequently utilized. The additional variability introduced by the pyrolytic process sometimes diminishes the precision of quantitative analysis. As in other analytical techniques, a calibration is usually necessary for the quantitation (see, e.g., [1]). The addition of an internal standard is possible and may improve the precision [2]. Direct pyrolysis/methylation performed directly in the injection port of a GC instrument is a particular technique very successfully used for quantitative analysis [3,4].

Besides its application as a tool for the analysis of polymers and composite materials, analytical pyrolysis is frequently utilized for the study of pyrolysates obtained from other materials exposed to heat. These materials may include non-polymeric molecules or mixtures of polymeric and non-polymeric molecules. A convenient way to evaluate the composition of pyrolysates is to use analytical pyrolysis equipment. Numerous examples of such applications will be discussed in Part 2 of this book.

Pyrolysis under controlled conditions is also used for synthetic purposes. Synthetic pyrolysis can be performed at laboratory or industrial scale. Industrial-scale pyrolysis has enormous economic implications, for example, for the oil industry and the waste processing industry. A discussion of industrial pyrolysis is beyond the purpose of this book, but in Part 2 there are some references to industrial applications of pyrolysis. Most commonly, the pyrolysis for synthetic purposes at laboratory scale is done in flow mode, when the substance to be pyrolyzed is passed through the hot zone in a flow of diluting gas. The optimization of the conditions for synthetic pyrolysis strongly depends on the chemical nature of the pyrolyzed substances and the goal of the process.



Simulation of specific processes that take place at elevated temperatures is another area where experimental pyrolysis is utilized. These processes may be related to industrial applications, understanding of accidental occurrences involving fire, testing of consumer products that may be exposed to high temperatures, etc. A variety of instrumental devices, some dedicated to a specific task and others for more diverse applications, were designed for simulating specific processes involving heating.

### **The choice of parameters for analytical pyrolysis**

The selected temperatures in analytical pyrolysis are usually between 350 °C and 950 °C because in this interval most organic compounds decompose completely. For special purposes this temperature can be higher or lower. The pyrolytic process is performed in a pyrolysis unit (pyrolyzer) that has a source of heat. The pyrolyzer is interfaced online or off-line with an analytical instrument, which is used for the measurement of the pyrolysis products. Common techniques applied for this purpose include GC, GC/MS, and MS. Pyrolysis GC/MS (Py-GC/MS) is probably the most common technique in analytical pyrolysis.

Analytical pyrolysis is typically performed as *flash pyrolysis*. This is carried out with a fast rate of temperature increase (of the order of 10,000 °C/s), geared toward reaching isothermal conditions at a temperature where the sample is completely pyrolyzed. After the final pyrolysis temperature is attained, the temperature is maintained essentially constant (*isothermal pyrolysis*).

Special types of analytical pyrolysis are known. One example is *fractionated pyrolysis*, in which the same sample is pyrolyzed at different temperatures for different times in order to study special fractions of the sample. Another special type is *stepwise pyrolysis*, in which the sample temperature is raised stepwise and the pyrolysis products are analyzed between each step. *Temperature-programmed pyrolysis* is another special type in which the sample is heated at a controlled rate within a temperature range. This type of pyrolysis can be used for analytical purposes but is not very common.

The pyrolysis is performed in a pyrolyzer that usually consists of a controller module and a pyrolyzing module. The controller provides the appropriate energy needed for heating. A primary requirement for the pyrolysis units is that of reproducibility [5,6]. One condition for achieving reproducibility is to use a precisely controlled temperature [7,8]. The targeted isothermal condition for flash pyrolysis is referred to as *equilibrium temperature* ( $T_{eq}$ ). The  $T_{eq}$  is also named *final pyrolysis temperature* because, in practice, it is not possible to heat a sample instantly to  $T_{eq}$ , although very short times for reaching  $T_{eq}$  can be achieved. Because pyrolysis is frequently a complex process, there is no precise rule to indicate which  $T_{eq}$  temperature should be chosen for a given sample. This value may depend on the material to be pyrolyzed and the scope of the analysis. The ceiling temperature  $T_c = \Delta H^\circ / \Delta S^\circ$  (see rel. 3.1.22) or kinetically required temperature  $T_k$  (see rel. 3.2.20) may be used as guides for choosing  $T_{eq}$ . The ceiling temperature  $T_c$  is easier to calculate but it has not proven, in practice, to be a very good estimation for  $T_{eq}$ . On the other hand,  $T_k$  is not easily calculated. For this reason, in the specialized literature the description of the pyrolysis products of a certain material is almost always associated with the description of experimental conditions for the pyrolysis including the value for  $T_{eq}$ .

Another parameter selected for analytical pyrolysis experiments is the *temperature rise time* (TRT). This parameter measures the time necessary for the heating element of the pyrolyzer to reach  $T_{eq}$ . Since different temperatures may favor the formation of different compounds, this parameter is very important since temperature varies during heating. Figure 4.1.1 shows the variation of residual mole fraction  $W/W_0$  as a function of temperature for 0.1 s heating time of two hypothetical reactions (one with  $A = 50,000 \text{ s}^{-1}$  and  $E^\ddagger = 20 \text{ kcal/mol}$  and the other with  $A = 500 \text{ s}^{-1}$  and  $E^\ddagger = 7.5 \text{ kcal/mol}$ ).

For a pyrolysis that targets  $T_{eq} = 800 \text{ °C}$  when the heating takes place slowly and the sample is kept at temperatures below 550 °C for a longer time, Figure 4.1.1 shows that the reaction with  $A = 500 \text{ s}^{-1}$  and  $E^\ddagger = 7.5 \text{ kcal/mol}$  is favored. For a rapid heating time that reaches  $T_{eq} = 700 \text{ °C}$  very fast, the other reaction is favored. Therefore, differences in the composition of pyrolysates may occur for different heating rates (usually expressed in °C/ms). The goal in flash pyrolysis is to have a very short TRT, such that the decomposition of the sample takes place, virtually, in isothermal conditions at  $T_{eq}$ . The isothermal conditions are usually easier to reproduce than a specified uniform heating. However, even this requirement may not be always simple to achieve for large samples or in pyrolyzers of specific

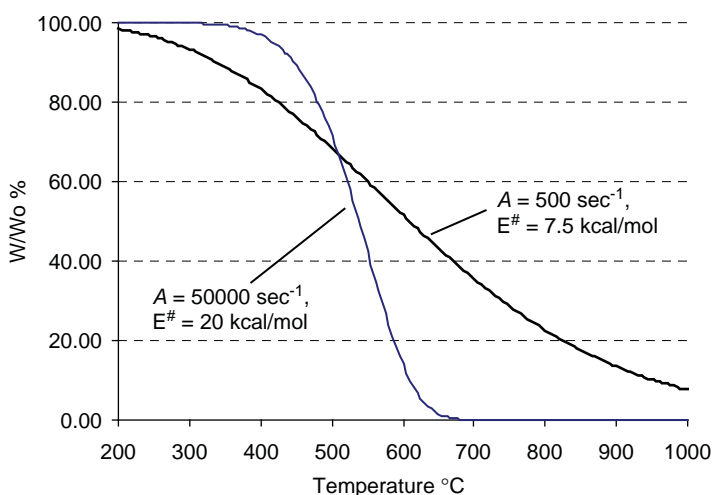


FIGURE 4.1.1. Variation of residual mole fraction  $W/W_0$  as a function of temperature for 0.1 s heating time of two hypothetical reactions with different  $A$  and  $E$  values.

construction since it takes time for the sample (and sample holder) to reach  $T_{eq}$ . During the temperature rise period (TRT) the sample is exposed to lower temperatures. When the increase in temperature is linear, its variation during the TRT can be expressed by the formula:

$$T (^{\circ}\text{C}) = T_0 + \beta t \quad (4.1.1)$$

where  $T_0$  is the initial temperature ( $^{\circ}\text{C}$ ),  $\beta$  the heating rate ( $^{\circ}\text{C}/\text{ms}$ ), and  $t$  the time (ms).

One more parameter used for the control of the pyrolytic process is the *total pyrolysis time* (or *total heating time*, THT), which is the sum of TRT and the time of maintaining the sample at  $T_{eq}$ . THT should be chosen long enough for the total amount of sample to be pyrolyzed. Longer THTs than those exactly needed for the pyrolysis of the sample are commonly used to assure that the whole sample is pyrolyzed. THT duration after the sample is pyrolyzed is usually not critical since the pyrolysates are swept by the carrier gas outside the high-temperature zone toward the GC instrument.

An important factor in achieving reproducibility in analytical pyrolysis is the pyrolyzer construction. Several pyrolyzer types are commercially available. Some unique setups have been developed and reported. Various types of common pyrolyzers used for analytical purposes are discussed in Section 4.2.

### **The choice of parameters in pyrolysis for synthetic purposes at laboratory scale**

Pyrolysis can be used as a technique for the preparation of specific compounds [9]. The pyrolytic procedures applied in the laboratory vary considerably regarding the heating temperature, pyrolysis time, pressure, amount of sample, and catalysts. The process can be run in a static manner or in a flow system. In a static procedure the sample can be heated under reflux, with the reaction products returning in the heated zone. This technique can be used only when the product of interest is considerably more stable compared to the reagent, since heating continues for the products as well as for the reagents. The heating temperatures for static pyrolysis are typically not very high (not exceeding about  $300^{\circ}\text{C}$ ). More frequently applied than static pyrolysis is flash pyrolysis [10], which uses short heating times (0.1–1 s) with the reagent passed through a heated tube in a flow of an inert gas or in vacuum. The vacuum pyrolysis may be performed at reduced pressure (1–30 mm Hg), moderate vacuum (0.01–1 mm Hg), or even very low pressure ( $10^{-3}$  mm Hg or less).

A special group of studies involving pyrolysis are those related to gas kinetics, where specific processes occurring in gas phase at elevated temperatures are assessed by pyrolytic techniques. Gas



kinetic studies may use pyrolysis times as short as milliseconds and may use dedicated instrumentation that is different from that used for synthetic purposes.

The heating temperature for synthetic purposes is adjusted to the specific purpose of synthesis. In Part 2 of this book, examples regarding the recommended temperature for specific reactions will be presented. The values for the heating temperature are typically between 350 °C and 950 °C, with unusual cases of lower or higher temperatures.

Besides temperature, the *contact time* (CT) or the length of effective heating time is another important factor in pyrolysis for synthetic purposes. The contact time for a flow process should be calculated considering a number of factors including the initial flow rate of the carrier gas, the expansion of the gas at the hot temperature, the formation of different gas species from one initial reagent, and the volume of the heated zone.

Although the heating temperature and contact time are very important, another parameter that must be considered in synthetic pyrolysis is the quenching time of pyrolytic reactions. While leaving the pyrolysis zone, the reaction products may continue to react and/or decompose, and the cooling of the pyrolysates may be an important step for obtaining the desired yield of a pyrolysis product. Specific recommendations may be made regarding how fast the reaction products of a pyrolysis reaction must be cooled, and a variety of trapping procedures are recommended in literature [11].

One additional factor that is used for achieving a specific synthesis is the use of packing materials and catalysts in the pyrolysis zone. When the reagent is passed through a heated tube containing a packing material, the residence time in the heated zone is increased. The packing can be an inert material (such as silica or Pyrex rings). However, alumina or porous silica beads may be used as packing, and, in this case, the potential catalytic effect of the solid support should not be neglected. Specific catalysts also can be included in the heated zone. One particular case of catalytic pyrolysis is using pyrolysis on a metallic filament. The temperatures achieved with a filament can be quite high (1200 °C or higher), the material of the filament also being important for its catalytic properties. Nickel, nichrome, or other filament materials can be used for this purpose.

Reagents added during pyrolysis are sometimes necessary for a specific purpose. For example, hydrogen and a platinum catalyst were used for thermal decomposition/hydrogenation of different materials [12]. Various types of pyrolyzers used in organic synthesis are discussed in Section 4.3.

### ***Adjustment of pyrolysis parameters to simulate a specific process***

Pyrolysis in well-controlled experimental conditions is very useful for understanding certain thermal processes. Among these the gas kinetics studies were previously mentioned, but other thermal processes can also be studied. A common thermal process simulated with pyrolytic instrumentation is burning. Burning is a complex process including combustion, volatilization, steam distillation, aerosol formation, etc., in addition to pyrolysis. Pyrolytic instrumentation can be used to evaluate not only the pyrolytic process, but also other components of burning, usually by adding oxygen and other gases during heating.

As an example, pyrolysis studies were used for the simulation of the processes taking place in a cigarette during smoking. The conditions of pyrolysis must simulate the conditions that occur in the burning zone of the cigarette. These conditions have been described in various papers [13] and include a dynamic heating rate of 2 °C/s during smolder period and up to several hundreds °C/s during puffing [14] in a range of temperatures from room temperature to above 900 °C, specific oxygen levels and gas flow rates over the pyrolyzing material, specific size of the sample, and specific residence time of the products in the high-temperature region. Among different procedures to simulate cigarette burning, a “pulsed” pyrolysis apparatus was designed [15] in which the tobacco was placed in a quartz tube, and then a heating block surrounding the tube was moved along the tube linearly. Other studies used common analytical pyrolysis instrumentation with specific heating conditions, pyrolysis atmosphere, and gas flows [16,17]. A set of such conditions recommended for analytical pyrolysis instruments is summarized in Table 4.1.1 [17].

The results of the simulated burning by pyrolysis were further compared to those previously obtained regarding, for example, the transfer in smoke of specific intact compounds from a burning cigarette, with

TABLE 4.1.1. *Pyrolysis conditions that mimic those in a burning cone of a cigarette and the rationale for their use [17]*

Condition	Rationale
Atmosphere 9% O <sub>2</sub> in N <sub>2</sub>	Approximate mean oxygen level throughout the pyrolysis/distillation zone inside the burning cigarette during a puff
Pyroprobe initial temperature of 300 °C held for 5 s	Simulation of tobacco ingredient heated in smolder period prior to puff
Pyroprobe ramp: 30 °C/s from 300 °C to 900 °C	Approximate mean heating rate throughout the pyrolysis/distillation zone during a puff, and the temperature range to which the cigarette burning zone is subjected
Pyroprobe final temperature of 900 °C held for 5 s	Maximum duration of high burning zone temperature during puff under extreme human smoking conditions
Sample size 200 µg for ingredient analysis, on quartz wool	Sample size similar order of magnitude for many tobacco ingredients. Quartz wool simulates tobacco strand structure
Total pyrolysis gas flow: 4.6 mL/s	Sweeps products out of the pyrolysis zone, as in an actual burning cigarette
Pyrolysis/GC interface temperature 250 °C	Prevention of condensation of pyrolysate in the interface

good results in many respects [17]. Other examples of simulated processes using pyrolysis are discussed in Part 2 of this book.

## 4.2. INSTRUMENTATION USED IN ANALYTICAL PYROLYSIS

### **General aspects**

Since analytical pyrolysis is a relatively common technique, a variety of dedicated instruments are available. These instruments allow a rapid heating of the sample to a specific temperature (short TRT), this temperature being maintained constant for a specific period of time. Pyrolysis is frequently performed on solid samples, but analytical pyrolysis of liquid or gaseous samples is also common. For liquid samples with high boiling point, pyrolysis using the same instrumentation as for solids can be performed. However, specific requirements are necessary in order to assure that the sample is pyrolyzed and not only evaporated. For gas samples or for liquids with lower boiling points, when analytical pyrolysis is performed with the purpose of studying the effect of high temperatures, special instrumentation must be used.

For common pyrolyzers used on solid samples or on liquids with high boiling point, besides the capability to perform a rapid heating and the maintenance of a specific temperature, another common capability is the controlling of the pyrolysis atmosphere. The stream of gas inside the pyrolyzer can be used further as a carrier gas if the pyrolyzer is interfaced, for example, with a gas chromatograph. The analytical pyrolytic instruments for solid samples are constructed such that a convenient transfer of the pyrolysate to an analytical instrument can be done. This transfer must be rapid, without losses, and accommodating the requirements of the analytical side (sample amount, volume, pressure, and nature of the carrier gas). Gas switching capability is an optional feature for some pyrolyzers. Pyrolysis in a specific atmosphere that is different from helium can be very useful in a number of practical applications, such as the study of burning. Some of the gases in which pyrolysis is performed, particularly oxygen, are not acceptable as a carrier gas for chromatography. For this reason, it is sometimes necessary to perform the pyrolysis in one gas (e.g., air, or nitrogen with 5–10% oxygen) and transfer the pyrolysates to the analytical instrument (GC or GC/MS) with another gas that is also used as a carrier gas in the chromatograph. A number of detailed descriptions for instruments used in analytical pyrolysis can be found in literature (e.g., [18,19]).

Pyrolysis of low-boiling-point liquids or gases can be studied in static systems, dynamic systems, and shock tubes [20]. Typically, these pyrolyzer types are hyphenated with an analytical instrument,

which can be a GC/MS or a spectroscopic instrument such as an IR spectrometer. Most of this section is dedicated to the description of pyrolyzers used for solid and high-boiling-point liquid samples. A subsection on pyrolyzers used for gases (and low-boiling-point liquids) is also included.

### **Resistively heated filament pyrolyzers for solid samples**

This type of pyrolysis unit usually consists of a controller and a pyrolyzing module (sometimes called a pyrolyzer). The controller provides the appropriate electrical energy needed for heating. A simplified scheme of a pyrolyzer (based on the design of a flash heated filament system made by CDS Inc.) is shown in Figure 4.2.1. The pyrolyzer body or the housing (see Figure 4.2.1) consists of a small chamber that is heated in order to avoid condensation of the pyrolysates on the housing walls. The housing temperature,  $T_{\text{hou}}$ , is typically around 200–280 °C, and its walls are not in contact with the sample. Inside the pyrolyzer housing, a probe insert can be introduced or removed. The tip of the probe insert has the heating element and a sample holder. The heating element consists of a coil or a ribbon filament (typically made from platinum) that can reach the desired pyrolysis temperature when electrical current from the controller is passed through it. The sample holder is usually a quartz tube or boat where the small sample is deposited for analysis. A stream of inert gas flows through the housing carrying the pyrolysates to the analytical instrument.

The heating energy for this pyrolyzer is generated by an electric current passing through a resistive conductor that produces heat in accordance with Joule's law:

$$Q = I^2 R t = \frac{V^2 t}{R} \quad (4.2.1)$$

where  $Q$  is the amount of heat (J),  $I$  the current intensity (A),  $R$  the electrical resistance of the conductor (Ohms),  $t$  the time in s, and  $V$  the voltage (V). The temperatures reached by filament pyrolyzers can go up to about 1400 °C, although temperatures between 350 °C and 950 °C are used more frequently. A simple flash pyrolysis unit that operates at a fixed voltage could be constructed easily. However, such a unit operating within common values for the current intensity and voltage will have a TRT that is too long to be appropriate for flash pyrolysis. Systems with boosted current or boosted voltage are used to achieve more rapid heating [21]. These systems apply a constant current with an initial boost pulse to the filament for ensuring a rapid temperature increase at the beginning of the heating period. Values for TRT as low as 7 ms from ambient to 1000 °C have been reported for a filament pyrolyzer [19]. The ideal variation of temperature for the filament is a step curve [18], but deviations from that profile are not uncommon. The true temperature of a sample heated using a filament pyrolyzer can be quite different from the ideal profile of temperature and increases even more slowly inside the samples [22]. In order to obtain a correct  $T_{\text{eq}}$ , modern equipment uses a feedback controlled temperature system (see, e.g., [18] for a more detailed description of this type of pyrolyzer). Several other procedures for a precise temperature control of the filament are available, such as the use of optical pyrometry or

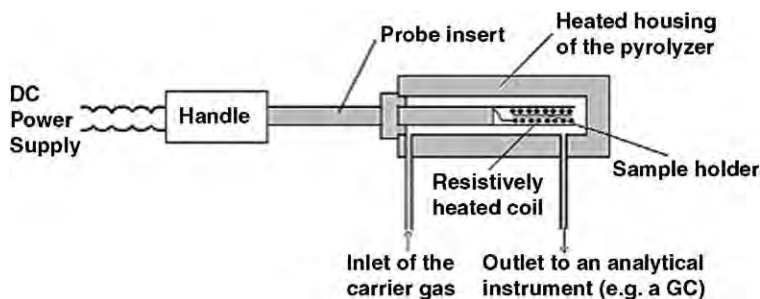


FIGURE 4.2.1. The simplified scheme of a pyrolyzer (based on the design of a heated filament system made by CDS Inc.).

thermocouples [23,24]. Special pyrolysis systems that allow programmed heated rates at different time intervals are also available (e.g., [25]), including a system that uses computer-driven feedback control for the heating system and can apply virtually any time–temperature history to the sample [26].

There are several advantages of the resistively heated filament pyrolyzers compared to other types. They can achieve very short TRT values, the temperature range is large, and  $T_{eq}$  can be set at any desired value in this range. Several commercially available instruments are capable of performing programmed pyrolysis.

Some problems are inherent to this type of pyrolyzer. One such problem is that the set temperature and the actual temperature of the filament must be calibrated. The filament electrical resistance is part of the temperature controlling circuit. This resistance may modify in time, mainly in the systems where the sample is put directly on the filament. Because of this, the correspondence between the set operating temperature and the actual temperature will change during the life of the filament. Even in correctly operating instruments, problems may occur in achieving the  $T_{eq}$  as precisely as the manufacturer may indicate [27]. Another problem with filament pyrolyzers is the possibility that the filament may be nonuniformly heated over its length. This may determine different  $T_{eq}$ 's in different points of the filament. If the sample is not always placed at the same point of the filament in repeated experiments, this may introduce some variability. In spite of these disadvantages, since they are simple and have overall good reproducibility, the resistively heated filament pyrolyzers are among the most commonly used for analytical pyrolysis (e.g., [28]). Some filament pyrolyzers also have multiple sampling capability (autosampling) that further increases the ease of their utilization.

### **Curie point pyrolyzers**

Ferromagnetic conductors can be rapidly heated by interaction with a high frequency (radio frequency, RF) electromagnetic field. The sample to be pyrolyzed can be placed in close contact with the conductor, which can be shaped into different forms such as a wire, ribbon, folded ribbon, or cylinder to properly hold the sample. The sample and its holder are maintained in a stream of inert gas in a similar way as for resistively heated filaments. The housing where the sample and its ferromagnetic holder are introduced is also heated to avoid the condensation of the pyrolysate but without decomposing the sample before pyrolysis. The heating of the conductor and subsequently of the sample can be realized with a short TRT, commonly between 10 ms and 100 ms. Eddy currents in the conductor surface (skin) and hysteresis losses due to changes in the magnetic polarity cause the temperature to increase rapidly when the conductor is placed in the high-frequency electromagnetic field. The increase in temperature is, however, limited for these ferromagnetic conductors to the Curie point temperature [29]. This is a temperature specific for each material at which the transition from ferromagnetic to paramagnetic properties occurs. In this way, besides a rapid heating, a well-defined end temperature is attained. This end temperature (Curie point) depends on the composition of the ferromagnetic metal or alloy, and lists of Curie point temperatures for various alloys are available in literature [18] or provided by the instrument manufacturers (e.g., [30,31]). The temperatures obtained with Curie point instruments cannot be varied continuously and are set by the choice of the alloy type of the heating element.

Commonly, the power outputs range from 100 W to 1500 W. The rate of temperature rise depends on the conductor mass and specific heat, as well as on the power consumption of the ferromagnetic conductor. This power consumption per unit surface is related to the amount of heat generated by the conductor and implicitly to the temperature. More detailed descriptions of the parameters implicated in the heating of a ferromagnetic conductor located inside a high-frequency induction coil are found in literature [18,29].

The Curie point pyrolyzers have several advantages when compared to other systems. The TRT is usually very short and the heating rate is reproducible. The  $T_{eq}$  temperature is accurately reproducible for the same alloy. On the other hand, the set temperatures can be only discrete and are limited to the values offered by different alloys. Even though the direct contact of the sample with the ferromagnetic alloy offers the advantage of a good heat transfer, it can be a source of catalytic interferences. For this reason some suppliers offer gold-plated ferromagnetic sample holders. Autosampling capability is also available for some Curie point pyrolyzers [18].

### **Furnace pyrolyzers for analytical pyrolysis of solid samples**

Furnace pyrolyzers are devices used in both flash pyrolysis and slow gradient pyrolysis. For flash pyrolysis, the common principle of use is to keep the furnace at the desired temperature and suddenly introduce the sample into the furnace. The heating of the furnace is commonly done using electrical heating, which can be controlled using thermocouples and feedback systems to maintain the correct temperature. An inert gas flow is commonly passed through the furnace to sweep the pyrolysis products into the analytical instrument. For analytical purposes it is, therefore, preferable to have small furnaces with low dead volumes, such that the gas flow can be kept at relatively low values. On the other hand, if the mass of the furnace is small, the sample introduction may modify the furnace temperature. Several designs were used for furnace pyrolyzers, a successful one being a vertical furnace that allows the sample to be dropped from a cool zone into a heated zone (e.g., the SGE micro-furnace Pyrojector [32]). A modified diagram of a micro-furnace pyrolyzer is shown in Figure 4.2.2 [33].

The operation of the instrument shown in Figure 4.2.2 takes place as follows: (1) The sample in a small quartz tube is introduced in the inlet of the pyrolysis device. The loading valve spindle and solenoid valve of the vent are closed, and the carrier gas flows upward. (2) The loading valve and the vent are opened, but the upward gas flow supports the sample vial and prevents it from entering the heated zone. (3) The vent is closed and the switch valve changes the flow of the carrier gas downward; the sample drops into the heated zone where it is kept for a desired time. (4) The vent is opened and the switch valve changes the flow of the carrier gas upward; the pyrolyzed sample is ejected from the heated zone. (5) The valve spindle rotates into the closed position. Switching between the gas in which the pyrolysis takes place and the carrier gas can be achieved using a second carrier gas inlet and an additional switch valve.

The micro-furnace pyrolyzer shown in Figure 4.2.2 allows a complete elimination of the traces of air that may be included in the pyrolysis atmosphere when the sample is introduced into the device. Also, a simple modification of the design allows switching between the gas in which the pyrolysis takes place and the carrier gas.

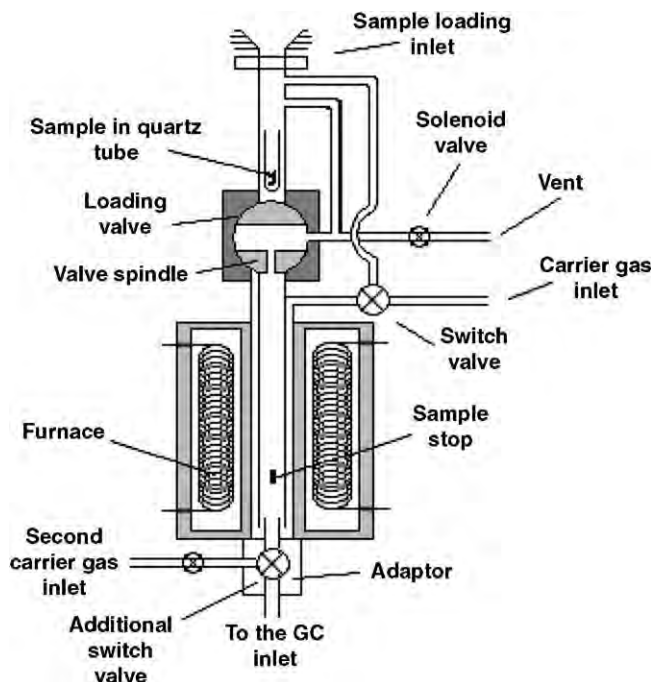


FIGURE 4.2.2. Simplified schematics of a micro-furnace pyrolyzer [33] (see text for details).

Achieving short TRT values is more problematic in furnace pyrolyzers as compared to other pyrolyzer types. A slow sample introduction in the hot zone of the furnace will result in a long TRT. A poor contact between the sample and the hot source also may lead to long TRT, most of the heat being transferred by radiation and convection, and not by conduction. However, fairly short TRTs in furnace pyrolyzers were reported in literature [34,35]. In furnace pyrolyzers it is more common to see differences in the temperature of the furnace and that of the sample. Due to the poor contact between the sample and the hot source, the sample may reach a lower actual temperature than the temperature of the furnace wall. This may be the explanation why there were reported variations in the pyrolysis products in micro-furnace systems as compared to the results obtained in inductively or filament heated pyrolyzers [36,37]. As an example, in the study done on the isoprene/styrene copolymer Kraton 1107 [36], the decomposition was found linear for the oven temperature and the ratio of two monomers (styrene and dipentene) only in a temperature range from 450 °C to 625 °C, which is narrower compared to that found for a filament or Curie point pyrolyzer.

Micro-furnace pyrolyzers are used successfully when larger amounts of sample need to be analyzed. This is needed sometimes for the pyrolysis of nonhomogeneous samples when a few milligrams of sample do not represent well the average sample composition, or when a larger amount of pyrolysate must be generated in order to analyze specific trace components. Slow gradient pyrolysis (at programmed rates) can be performed easily with furnace pyrolyzers, but rapid programmed heating is more difficult to achieve. A system using a programmable temperature vaporization (PTV) injector has been used successfully [38] for programmed heating in two different steps, one at 200 °C and another at 450 °C. The heating gradient, however, was slower than 8 °C/s. Slow gradient temperatures are commonly used in a series of thermal analysis instruments that are equipped with programmable furnaces. However, these thermoanalytical techniques are sometimes classified separately from pyrolysis, as previously indicated. Other different models of furnace pyrolyzers have been reported in literature [39]. As an example, a two-temperature zone furnace was made, and it was used to provide information about more volatile compounds trapped (adsorbed) in a sample as well as for performing true pyrolysis. In this system, the sample is heated first at 300 °C where the volatile compounds are eliminated, and then the sample is pyrolyzed at 550 °C.

Sealed vessel pyrolysis is another pyrolysis type that is performed in furnace-type pyrolyzers. In this type of pyrolysis, the sample is heated for a relatively long period of time in a sealed vessel generally at relatively low temperature (below 350 °C). High-temperature pyrolysis in sealed Vycor glass tubes also has been reported [40]. The pyrolysis products are analyzed further, commonly by off-line procedures (GC, GC/MS, FTIR, etc.). The technique allows the pyrolysis to be performed for as long as months and to use different atmospheres (inert or reactive) [41]. The procedure can be used as a preparative pyrolysis technique in addition to its use for analytical purposes. Also, not only solid samples can be pyrolyzed in a sealed tube, the procedure can also be used for liquids and even for gases, taking the appropriate precautions to avoid exceeding pressures that could break the tube at higher temperatures.

### ***Radiative heating (laser) pyrolyzers***

Laser pyrolyzers are practically the only type of radiative heating pyrolyzer with applicability. Attempts were made in the past to use a strong light/heat source and focus the beam with lenses [42] to achieve the desired power output. However, the laser as a radiative energy source is much more convenient. The laser beam can be focused onto a small spot of a sample to deliver the radiative energy. This provides a special way to pyrolyze only a small portion of a sample. Various laser types were used for pyrolysis purposes: normal pulsed, Q-switched, or continuous wave (cw) [43], at different energy levels. More common are the normal pulsed high-power lasers. Some instruments use condensing lenses to enhance the energy delivered to a small area of the sample.

A range of energies can be transferred to the sample by the laser. For a spot of about 1 mm diameter, a typical pulsed laser used for pyrolysis can generate a mean power density of 0.2–2.0 MW/cm<sup>2</sup>. This high energy is partly absorbed by the sample when a rapid volatilization and decomposition take place. A plume is commonly generated along the axis of the beam, and more radiative energy is absorbed in this plume.



The theory of thermal aspects of laser desorption has been developed for a substrate surface subjected to pulsed laser irradiation, assuming that the laser intensity has a Gaussian distribution [44]. The given surface is covered with the organic layer, which does not absorb the laser energy. However, the heat flux in the substrate that absorbs the energy heats the sample to the same temperature as the substrate. The temperature of the plume may rise fairly high, and values as high as 10,000 °C are reported. However, more reasonable values range from 500 °C to 2000 °C. At temperatures as high as 2000 °C, only some stable radicals will exist. Therefore, the part of the sample taken into the plume will generate after cooling only noncharacteristic small molecules such as acetylene. The free radicals in the plume may produce unexpected secondary reactions. However, enough heat is transmitted by the hot plasma around the focus point of the laser. This heat will produce pyrolysis products similar to those generated by other pyrolysis techniques since equivalent temperatures are available. Some secondary reactions may take place between these pyrolysis products and the free radicals from the plume.

The maximum energy of the laser can be higher than needed for the pyrolysis purposes and needs to be attenuated. For a cw laser with a nominal energy of 100 W, the output has to be attenuated by operating the laser at about 10 W and splitting the beam. Usually, a laser micro-pyrolysis instrument includes a microscope used for the inspection of the area to be analyzed, allowing the beam to be focused on the portion of interest on the sample. The laser beam is split (and attenuated) in the microscope by using a semitransparent mirror, which allows control of the percent of the beam intensity that reaches the sample (5–15%). For a cw laser, powers between 0.5 W and 5 W with exposures varying from 1 s up to 5 min have been utilized for pyrolysis. The surface of the area exposed to the laser has varied from 20  $\mu\text{m}^2$  to 400  $\mu\text{m}^2$ . Other instruments use an alignment laser for locating the point on the sample where the pyrolysis should be performed. The alignment laser is optically positioned at the same spot as a high-energy pulsed laser that provides the energy necessary for the pyrolysis.

Besides the formation of some unusual products due to secondary reactions, there are several other problems regarding the use of lasers as an energy source for pyrolysis. A first problem is related to the absorption of the radiative energy into the sample. Transparent samples do not absorb the radiative energy properly. For this reason, several procedures were utilized to make the sample more opaque. One such procedure consists of adding powdered graphite [45] or a metal powder such as nickel [46] into the sample. This addition, however, can modify the course of the pyrolysis by catalytic effects or side reactions. A different procedure consists of depositing the sample in a very thin layer on a support that absorbs the radiation generating heat. In particular, a blue cobalt glass rod has been used [46] as a support for the sample, with temperatures attaining 900–1200 °C. Another problem with lasers is the difficulty of knowing precisely the equivalent temperature of pyrolysis. Due to some inherent characteristics of laser pyrolysis, its reproducibility is not always high.

A typical characteristic of laser pyrolysis is that it can achieve very short TRT times and also very short cooling times, in the range of 100–300  $\mu\text{s}$ . This will contribute to the uniqueness of the degradation conditions for laser pyrolysis, which are rather different from the other types. In addition to this, the capability to pyrolyze only a very small area of the sample is characteristic for most laser pyrolyzers. This directional nature can be of exceptional utility when combined with microscopic inspection of a particular sample. Inclusions in the samples, for example, can be analyzed successfully with this technique.

On the other hand, deliberate defocusing of the laser beam was studied [47] in order to cover a wider area on the sample. Several alternative approaches were examined in order to provide more detailed information on the sample. For the study of the order of formation of specific molecular fragments during thermal degradation, for example, a time-resolved laser-induced degradation was applied [48]. In addition, attempts were made to use specific wavelengths corresponding to a given vibration of the molecule in order to break specific bonds, using lasers as a source of energy.

Besides conventional laser pyrolysis, several other techniques were developed around the concept of evaporating the sample using a laser beam. However, most of these techniques were developed with the purpose of preserving the structure of the analyte while transferring it into an ionized gas form. Techniques such as matrix assisted laser desorption/ionization (MALDI) [49–52] are commonly used for the analysis of biopolymers. However, MALDI does not (or is not intended to) produce pyrolysis of the analytes and cannot be classified as a pyrolytic technique.

### ***Other pyrolyzer types for solid samples***

Besides the previously described pyrolyzer types, others have been constructed and reported in the literature [34,53,54]. Some are based on variations of typical pyrolyzer systems. One such system uses a micro-furnace pyrolyzer with the capability to hydrogenate the pyrolysis products. For this purpose, the system uses hydrogen carrier, and, in line with the micro furnace, it has a catalyst column containing a solid support with Pt-catalyst (and a precolumn portion to trap nonvolatile pyrolysis products) [55].

Other techniques, such as photolysis [56], were utilized for breaking down organic molecules for further analysis. However, these cannot be considered as pyrolytic procedures. A theoretical approach has been developed [56] to compare mass spectrometric, thermolytic, and photolytic fragmentation reactions.

Alternative techniques for performing pyrolysis are described in literature. An example is the “in column” pyrolysis [57], where pyrolysis is carried out in a segment of deactivated stainless steel tubing inserted between the injection port of the GC and the analytical column. The procedure assures that all pyrolysis products that can go through the chromatographic column are analyzed and no losses by condensation take place, for example, in the housing of the pyrolyzer. One disadvantage of this technique is that each sample loading is done on a replaceable piece of steel tubing, which must be mounted and dismounted in the gas chromatograph for each sample.

### ***Instrumentation for the analytical pyrolysis of gases and low boiling compounds***

Pyrolysis of gases and low-boiling compounds, followed by the analysis of the reaction products, is typically performed with the purpose of understanding the formation of specific reaction products, study of reaction mechanisms, and/or determination of specific thermodynamic and kinetic parameters of the process. Both static and dynamic systems can be used for this purpose.

In static systems, the parent compound is typically heated in a sealed container at a selected temperature and for a specific length of time. An example of such a system consists of a quartz cylinder of about 500-mL volume that is heated in a cylindrical furnace. The inside of the reaction vessel should be very clean and inert. Special measures are taken to assure that no external gas diffuses into the cylinder at elevated temperatures. For this purpose, the reaction vessel is sometimes included in another quartz tube, and an inert gas is passed through the annular space between the outer tube and the inner pyrolysis chamber. The pyrolysis chamber is connected to a vacuum pump, a feeding line, a vacuum gauge, and a sampling line, sometimes with the capability to trap the reaction products at very low temperatures (e.g., in liquid nitrogen). The pyrolyzer is typically heated at the desired temperature (precisely measured with thermocouples) while maintained under high vacuum. When the desired temperature is attained, the gas (or the liquid vapors) to be pyrolyzed is admitted into the pyrolyzer chamber and kept inside for a specified time. The analysis of the pyrolysis products can be done, for example, by sampling the content followed by GC/MS analysis. Other analytical procedures are also applicable [58].

Flow-through reactors (flow reactors or dynamic systems) are furnace-type pyrolyzers used mainly for the analysis of solids or liquids that can be easily vaporized. The equipment includes capabilities to measure precisely the temperature, the gas flow, and the gas pressure. A simplified scheme of a flow reactor is shown in Figure 4.2.3.

The reactor consists of an inert tube (e.g., made from quartz) introduced into an electrically heated tubular furnace, with the temperature precisely controlled. A constant flow of gas (or gases) is passed through a vaporizer and further through the quartz tube from the furnace. The parent substance is introduced into the vaporizer and kept at the desired temperature to generate a specific amount of vapors (with no decomposition). The vapors of the parent substance at a controlled concentration in the flow of gas are passed through the heated portion of the quartz tube in the furnace. Temperatures from several hundreds °C up to 1100–1200 °C can be achieved with this type of furnace. The residence time in the heated zone is calculated from the flow rate of gases, dimension of the heated tube, temperature of the furnace, and the potential changes in the number of moles of gas caused by the pyrolytic process. Pyrolysis products are either analyzed online, or collected and analyzed off-line. The systems can have the capability of evaluating the pyrolysis products of a parent compound in a mixture of gases,



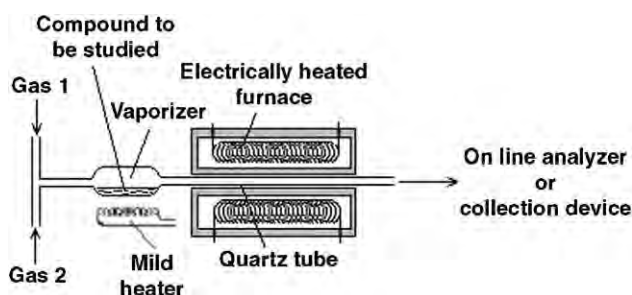


FIGURE 4.2.3. Simplified diagram of a flow reactor.

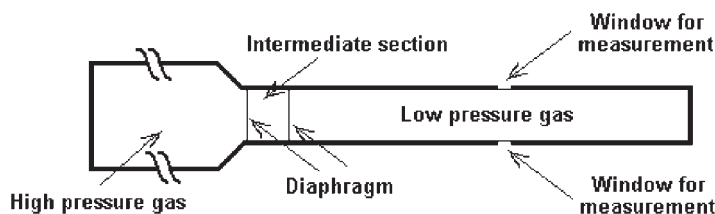


FIGURE 4.2.4. Simplified diagram of a shock tube.

for example, a diluent inert gas, and a specific content of oxygen. One disadvantage of flow systems is the difficulty of completely eliminating the reactions at the wall of the flow tube in order to ensure that only reactions in homogeneous phase take place [59]. Also, the temperature profile inside the reactor (flow tube) is not uniform, usually following a specific profile, with lower temperatures at the ends of the tube and higher temperature in the center. The reaction products are either analyzed online using IR, MS, GC/MS, or other analytical instrumentation or collected and analyzed afterward. The collection can be done using cryogenic devices, various types of traps, adsorbents, etc.

Pyrolysis in a flow reactor can require, for some compounds, the use of vacuum ( $10^{-3}$  to  $10^{-5}$  Torr). In such instances, a pyrolyzer similar to that shown in Figure 4.2.3 but connected to a vacuum system can be utilized. Detailed description of this type of pyrolyzer can be found in the literature [60,61].

Shock tube experiments were also applied for the study of pyrolysis of gases, when short exposure times at high temperatures (above 1000 °K) were employed [62–64]. A typical shock tube is a metal tube in which a gas at low pressure and a gas at a very high pressure are separated by a diaphragm, as shown in Figure 4.2.4. The tube dimensions and the length of the low-pressure and high-pressure sections can vary.

It is common to indicate the low-pressure gas as driven gas and the high-pressure gas as driver gas. The diaphragm separating the gases is eliminated suddenly (e.g., by rupture). The driver gas is allowed to burst into the driven gas, producing a shock wave that travels into the low-pressure section of the shock tube. An intermediate section sometimes is used to separate the high-pressure chamber from the low-pressure chamber. In one reported study [64], for example, the tube had a rectangular cross section ( $4.45 \times 6.35$  cm) with the high-pressure section of 2.4 m and low-pressure section of 6.1 m. The driven gas was at 7–49 Torr, and the calibrated diaphragms burst at fixed pressures between  $15 \times 10^3$  Torr and  $26 \times 10^3$  Torr applied in the high-pressure section. This shock wave increases the temperature and pressure of the driven gas and induces a flow in the direction of the shock wave. The behavior of the shock wave (density, speed, pressure) usually is calculated using Rankine–Hugoniot equation. Once the incident shock wave reaches the end of the shock tube, it is reflected back into the already heated gas, resulting in a further increase in the temperature and pressure of the gas. This can create a high-temperature and high-pressure zone in the driven gas. Depending on various parameters including the geometry of the shock tube and the pressure, temperature, and nature of the two gases, it is possible to calculate the achieved temperatures (see, e.g., [65]), the speed of the shock wave, and the pressure of the gas in a specific point. Even temperatures higher than 3000 °K can be achieved with shock tubes.

The driven gas and the driver gas can have the same composition or can be different. The analytical data can be collected during the heating of the gas in a measurement window, using, for example, IR emission or various light absorption techniques. Also, the gases can be analyzed after the experiment is finished, for example, by GC/MS. A number of technical details are associated with the construction of shock tubes [20]. For example, different techniques are used for bursting the diaphragm. The diaphragm must burst suddenly and in a reproducible manner in order to provide good test results.

### Online analysis of pyrolysates

Pyrolysates generated with one of the devices previously described are typically transferred in a flow of gas into an analytical instrument. The most common such instrument is a gas chromatograph/mass spectrometer. The typical chemical complexity of pyrolysates requires an efficient separation for the analysis, and that explains the common use of chromatography coupled with the analytical pyrolysis. Since low-molecular-mass fragments are frequently generated in the pyrolytic process, GC is the technique usually applied for the separation. The simplified diagram of a Py-GC instrument (not to scale) is shown in Figure 4.2.5.

The use of MS as the detection tool provides very good sensitivity, in addition to the identification capability. This sensitivity is necessary, mainly because the amount of sample used in analytical pyrolysis is very small (up to a few milligrams). Also, the analysis of trace components in pyrolysates is possible only by use of very sensitive detection such as that offered by MS. The qualities of Py-GC/MS make this technique the most convenient and widely utilized in practice. Various ionization techniques applied in association with Py-GC/MS are reported in the literature (e.g., [18]). However, the most common ionization method is electron impact with the detection of positive ions (EI+). The chemical ionization (CI) is used sometimes, but CI spectra interpretation is difficult because of the lack of fragmentation and because the reproducibility in CI can be affected by the experimental conditions in which the spectra are generated. CI spectra provide valuable information regarding the molecular mass

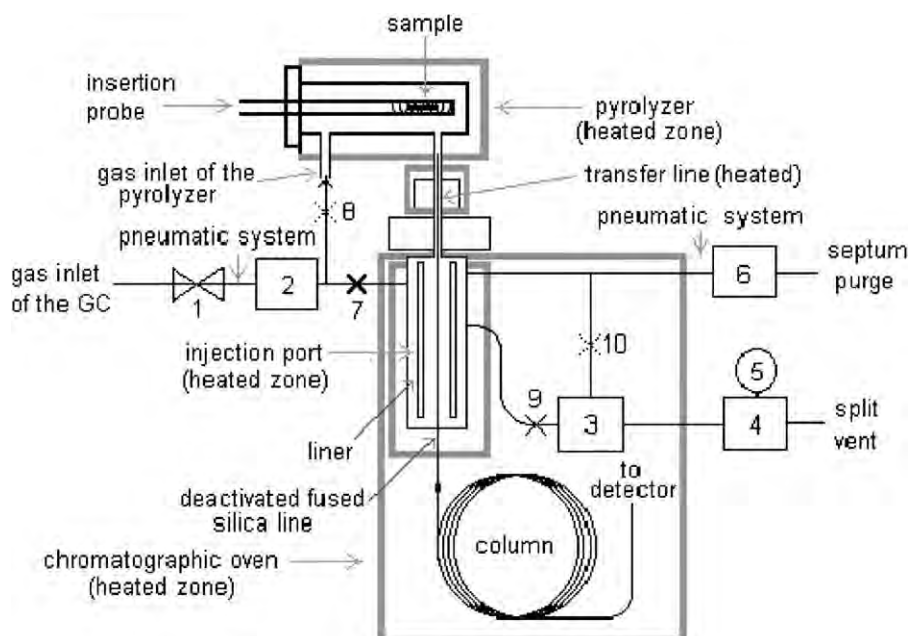


FIGURE 4.2.5. Simplified diagram of a Py-GC instrument (not to scale). The pneumatic system is as follows: (1) a mass flow controller, (2) electronic flow sensor, (3) solenoid valve, (4) back pressure regulator, (5) pressure gauge, (6) septum purge controller, (7) and (8) toggle connections to Py or GC, (9) and (10) toggle connections split/splitless for GC modes.

of the analyte, and this can be very useful in combination with EI<sup>+</sup> spectral information. Resonance enhanced multiphoton ionization (REMPI) also was used as a selective ionization technique associated with the analysis of pyrolysates, typically followed by mass spectrometric analysis, for example, using a time-of-flight (TOF) instrument [66,67]. For analytical purpose, REMPI also can be hyphenated with kinetic energy analysis of the resulting photoelectrons (REMPI-photoelectron spectroscopy or REMPI-PES). In REMPI, a tunable laser is used to generate molecules in an excited intermediate energetic state followed by the use of another photon beam that ionizes the molecules. The light intensity to achieve a typical multiphoton transition is generally significantly larger than the light intensity to achieve a single-photon photoabsorption. An ion and a free electron will result if the photons have imparted enough energy to exceed the ionization threshold energy of the molecule. Since the absorption wavelength and the excitation energy are specific for each molecule, REMPI generates ions only from a selected molecular species. The ions formed by this technique are analyzed further by a mass spectrometer (REMPI-MS) or with REMPI-PES.

The chromatograms resulting from the analysis of a pyrolysate commonly are indicated as pyrograms. Peak identification in pyrograms is usually done with the help of the search capability of mass spectrometer software and the mass spectral libraries (e.g., NIST/EPA/NIH 2005 or earlier versions, Wiley Registry of Mass Spectral Data 7th edition or earlier versions). The development of large libraries with standard spectra (over 444,000) and of algorithms for automatic library searches made the use of these tools for spectra interpretation routine. The algorithms for automatic library searches use several criteria for evaluating the quality of a match between the unknown spectrum and a reference spectrum. One well-known algorithm is the Probability Based Matching (PBM) system. This algorithm compares the unknown with all the spectra in the library and has two characteristic features: it weighs the mass peaks and performs a reverse search. The reverse search refers to the fact that the algorithm checks whether a peak from the reference spectrum is present in the unknown and in the appropriate abundance. The reverse search ignores peaks in the unknown that are not present in the reference.

Extensive identification of pyrolysate components may also require the chromatographic separation to be done in conditions that allow the elution of compounds with higher molecular weight or with high polarity. This is not always a simple task, since the types of chromatographic columns that allow the elution of heavier molecules typically do not offer good separation for the early eluting peaks. Also, the mass spectral identification of compounds with higher molecular weight is frequently more difficult than that of lighter compounds since fewer spectra for large molecules are found in the commercial mass spectral libraries. The extension toward higher molecular masses in the range of compounds identified in Py-GC/MS can be done by other procedures, such as derivatization of the pyrolysate (methylation with TMAH for acidic compounds, silylation for alcohols, etc.) or application of specific techniques dedicated for the analysis of a particular class of compounds (e.g., [1]) suspected to be present in the pyrolysate. Positive peak identification should be done using authentic compounds with the verification of the retention time in specific chromatographic conditions as well as the mass spectrum. However, very seldom is this practiced for the identification of the compounds in a pyrolysate.

The use of online Py-GC, without the MS capability, is used less frequently for pyrolysate analysis, although the technique had a larger utilization in the past when mass spectrometry was less common. Peak identification can be done using standards in this case.

Py-GC/MS also has some disadvantages. Larger molecules generated following pyrolysis or molecules with high polarity are not easily detected and analyzed by this technique, and they may contain valuable structural information on the initial molecule or may be an important component in the pyrolysate regarding its toxicity. Also, for a complete analysis of the pyrolysates, the compounds associated with the char sometimes must be analyzed. These nonvolatile components are not transferred in a gas flow. For this reason, the use of Py-GC/MS may leave unsolved a series of structural problems or may lead to the misinterpretation of the pyrolysate composition. HPLC was utilized sometimes for the separation of larger compounds from pyrolysates. However, liquid chromatography, even coupled with MS, does not provide enough identification capability (unless a LC/MS/MS system is used) since very little fragmentation is generated in LC/MS and the identification of the molecular species in pyrolysates is less successful. Other techniques such as FTIR or even NMR can be utilized for the analysis of pyrolysates, but their lower sensitivity compared to mass spectrometry explains their limited usage.

In online Py-GC or online Py-GC/MS, the housing of the pyrolyzer is directly connected to a GC. This can be done with a short tubing (properly heated to avoid condensations) connected to the injection port of the GC instrument or with a piece of deactivated silica capillary column with one end in the pyrolyzer housing passing through the injection port of the GC and connected directly to the analytical GC column. The sample size and the flow of gas used in the pyrolyzer should match the requirements imposed by the GC/MS system. For this reason, analytical pyrolyzers are constructed such that there are no significant discrepancies with the GC requirements. Since pyrolysis is commonly performed in a flow of an inert gas, this is used typically as the carrier gas for the chromatography. For specific needs, pyrolyzers can have the capability to perform pyrolysis in a gas that is different from the carrier gas. In these cases a gas exchange is performed between the pyrolyzer and the GC. Detailed descriptions of specific online analytical instruments connected to pyrolyzers are available in literature (e.g., [18]). Besides the GC or GC/MS connected to pyrolyzers, other analytical instruments also are used for pyrolysate analysis. One such relatively common instrument is a mass spectrometer (without a GC). The direct connection of the pyrolyzer with a mass spectrometer can be used for special purposes such as the identification of short-lived species generated in the pyrolytic processes. However, the use of pyrolysis-mass spectrometry (Py-MS) as an analytical tool is less common than in the past (e.g., [1,18]).

### ***Off-line analysis of pyrolysates of solid samples***

The analytical pyrolyzers with typical small sample size capability and flash heating of the sample can be used as a stand-alone device (off-line from a measuring analytical instrument). The pyrolysates can be collected (e.g., in a cooled piece of an uncoated capillary column) and further analyzed. This may be necessary when the pyrolysate contains substances that cannot be eluted from a typical chromatographic column or require derivatization for analysis, or when repeated collections are necessary for accumulating enough material to detect specific traces in the pyrolysate. SPME (followed by desorption and GC/MS analysis) also was reported as used for the analysis of pyrolysates [68]. Derivatization of pyrolysates before the analysis is also a common practice. This can be done, for example, using bis(trimethylsilyl)-trifluoroacetamide (BSTFA) to obtain trimethylsilyl (TMS) derivatives from compounds having active hydrogens in the molecule such as alcohols, acids, etc. (see, e.g., [1]).

### ***Instrumentation used for the analysis of flame composition***

The study of the burning process is closely related to pyrolysis. In addition to the pyrolysis occurring in the adjacent zone of burning, it is common that a combustion process starts with a pyrolytic step with the formation of free radicals that further react with the oxygen in continuing the combustion process. The study of flames and pyrolytic processes taking place in a flame frequently is done using special techniques. One of these techniques is, for example, molecular beam mass spectrometry (MBMS). This technique is used to measure stable and radical species within flames (e.g., low-pressure laminar flames). To elucidate the kinetics of flame processes, it is necessary to identify key radical species and molecules and measure their populations. In molecular beam mass spectrometry, a sample of the plume is taken from a region where the flowing flame stagnates. A differentially pumped molecular beam system ensures that the sample is representative of the flame chemistry. The symmetry of the plume allows spatial maps to be made of the reactive species. For a thorough species evaluation, the MBMS instrument typically combines a time-of-flight mass spectrometer using single-photon vacuum ultraviolet (VUV) photoionization and a quadrupole mass spectrometer with electron-impact ionization. Single-photon, near-threshold ionization provides a means to minimize the formation of fragment ions, while identifying species by their ionization threshold and mass. Both radicals and molecular compounds are measured by an electron impact MS (EI-MS) technique. The system can be made compatible with the use of REMPI as ionization technique when higher selectivity is required. The TOF-MS may have an optional imaging detector to discriminate between parent and fragment ions based on spatial ion patterns. A simplified diagram of a MBMS system is shown in Figure 4.2.6 (see, e.g., [69]).

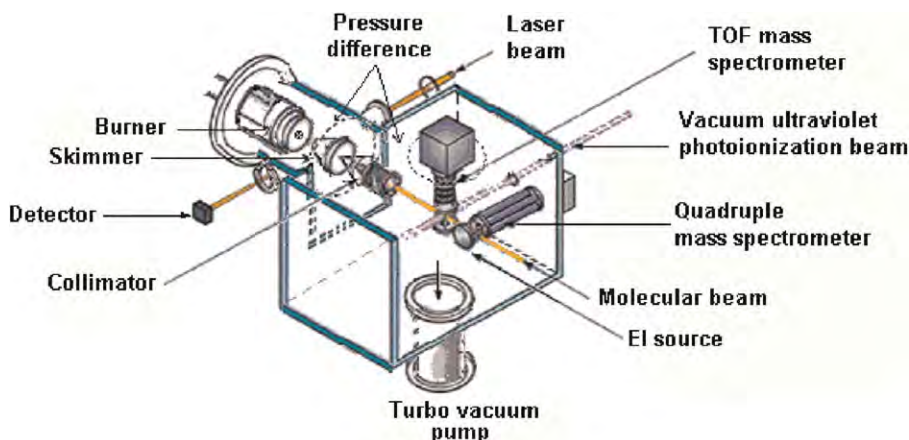


FIGURE 4.2.6. Simplified diagram of a MBMS system [69]. A special burner generates a steady flame. A molecular beam is obtained using a differentially pumped device. The plume is inspected using a laser beam. Analysis of the composition of the molecular beam is done by vacuum ultraviolet (VUV) photoionization with TOF-MS detection and using EI-MS (a quadrupole instrument).

### 4.3. INSTRUMENTATION USED IN LABORATORY PYROLYSIS FOR SYNTHESIS PURPOSE

#### *General aspects*

Pyrolysis performed for industrial synthetic purposes is a large independent field (e.g., [70,71]), and its coverage is beyond the purpose of this book. For laboratory purposes, specific types of pyrolysis setups were developed to be used for synthesis and are described in the literature (e.g., [9]). This instrumentation is typically assembled using common labware. For example, quartz or Pyrex tubes with or without an inert packing, laboratory furnaces, different types of flasks, funnels, condensers, joints, vacuum pumps, and vacuum measuring devices are used for this purpose. Specific dimensions and conditions for each instrument usually are described as details for the organic synthesis itself. Unlike analytical pyrolysis where manufacturers offer dedicated instruments, the variety of instruments used for pyrolytic synthesis is larger and less standardized. Only a few general types of instruments will be discussed in this section.

#### *Pyrolysis at atmospheric pressure*

Synthesis of some compounds does not require special precautions regarding an inert atmosphere, low pressure, or a very well controlled heating time for the reagent(s). Except for a heating source that is able to provide a higher temperature (a furnace), the equipment for this type of experiment is not different from that needed for performing simple organic synthesis. It typically includes a funnel as a reservoir for the reagent, a source of heat necessary for vaporizing the reagent, the “reactor” (which is typically a quartz or Pyrex tube with or without an inert packing), a condenser, and a collecting flask for reaction products. The reactor tube is heated in the furnace at the desired temperature. A simplified scheme of such an apparatus is shown in Figure 4.3.1 (see, e.g., [72]). In the apparatus shown in Figure 4.3.1, the reagent flows downward and is vaporized on the upper part of the reactor tube, which is hot. Therefore, in this setup, there is no need for an additional source for vaporizing the reagent. The temperature of the furnace is controlled, being measured, for example, with a thermocouple. A flow of inert gas is shown as a capability, although sometimes this is not necessary. However, the contact time, which is an important parameter in many pyrolytic synthesis, is acceptably controlled using a flow of gas, while an uncontrolled flow of the reagent in the hot zone of the reactor may lead to undesired further decomposition of the reaction products, excessive char formation, etc.



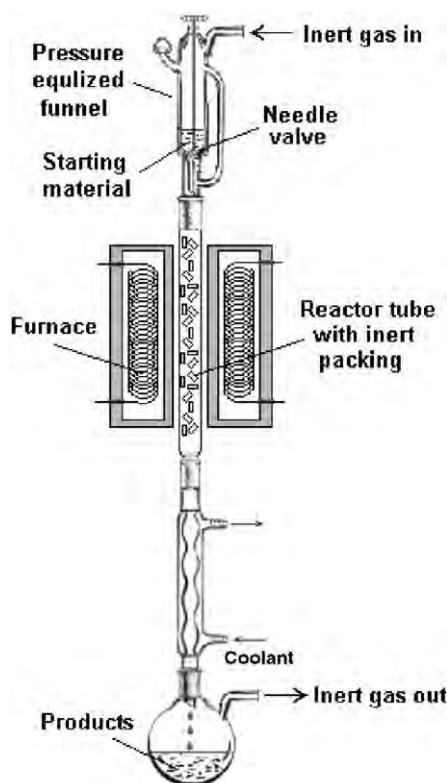


FIGURE 4.3.1. Drawing of an apparatus for pyrolytic synthesis at atmospheric pressure.

Many other alternative designs for similar setups are reported in the literature [9]. These include pyrolyzers with the flow of the reagents upwards, with no packing in the reactor tube, with catalytic packing in the reactor tube, or with collection of the reaction products in the upper part of the reactor (from the distillation process).

### **Pyrolysis at reduced pressure**

Pyrolysis at reduced pressure is probably more common than pyrolysis at atmospheric pressure. Depending on the requirements of the synthetic procedure, a considerable number of instruments can be used and are described in the literature [9]. A simplified drawing of an apparatus used for pyrolysis at reduced pressure is shown in Figure 4.3.2. In this apparatus, the sample is evaporated by heating at a specified rate. The reaction takes place at a recommended temperature and at a low pressure obtained using a vacuum pump and monitored with a vacuum gauge. This type of apparatus can be used for pyrolyzing gram quantities of materials [73]. Figure 4.3.2 shows an apparatus for pyrolytic synthesis for which many variants are reported in the literature (e.g., [9]).

Each modification aims to achieve specific characteristics. For example, rapid cooling of the reaction products may be necessary, and in this case the distance between the reactor and the condenser must be very short and the cooling temperature must be chosen very low (using, e.g., liquid nitrogen as a coolant). In addition, the flow of a carrier gas over the sample can be controlled in order to achieve a desired residence time of the sample at the pyrolysis temperature.

High pyrolysis temperature may be necessary, and a heating filament in direct contact with the reagents may be used for this purpose. An internal heating filament may play the additional role of a catalyst. A simplified model of such an apparatus is shown in Figure 4.3.3.

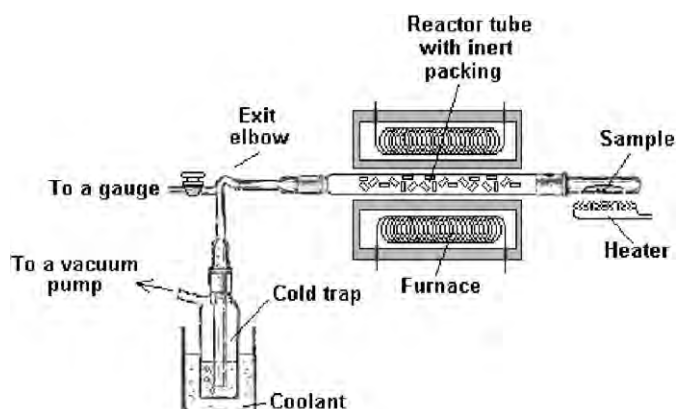


FIGURE 4.3.2. Simplified drawing of an apparatus for pyrolytic synthesis at reduced pressure.

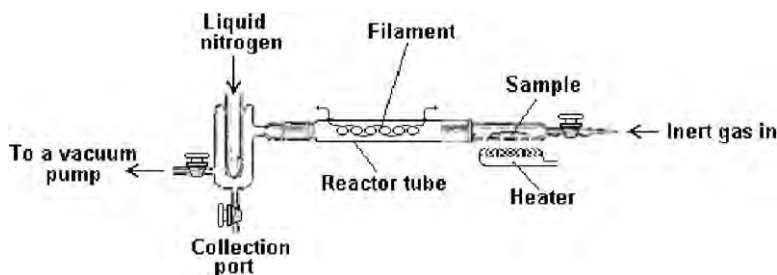


FIGURE 4.3.3. Simplified drawing of an apparatus for pyrolytic synthesis at reduced pressure with rapid cooling of reaction products, filament heating, and controlled flow of an inert gas in the reactor.

The pyrolysis performed at low pressure and with a short time of contact for the reagent with the high-temperature zone is typically described as flash vacuum pyrolysis (e.g., [74]). Different designs for the instrumentation used for flash vacuum pyrolysis can be found in the literature (e.g., [61,75]).

#### 4.4. INSTRUMENTATION USED TO SIMULATE A SPECIFIC PYROLYTIC PROCESS

##### *General aspects*

Pyrolysis at laboratory scale frequently is used to simulate different types of burning or industrial processes involving pyrolysis. Industrial applications of pyrolysis mainly related to petrochemical industry, such as oil processing using catalytic reformation/hydrogenation, are of enormous practical importance. A considerable volume of information is available in this field including books [76], scientific papers [77], and numerous patents [78]. Some basic information regarding the chemistry of processes used in petrochemical industry is discussed in Part 2, but the technical details regarding this subject are beyond the purpose of this book. Complex engineering problems also are related to waste incinerators, and various aspects of the process can be studied using laboratory reduced scale setups or even computer modeling [79].

Dedicated instruments for the study of burning of specific substances are available. One such instrument allows pyrolysis of small amounts of material (analytic scale) in a moving heated zone, simulating the advancing of a burning zone. The simplified diagram of such an instrument (based on CDS Pyrobot system [28]) is shown in Figure 4.4.1. Different atmospheres can be selected for pyrolysis, and the use of enough oxygen in the heated zone may lead to actual burning of the sample. A pyrolyzer

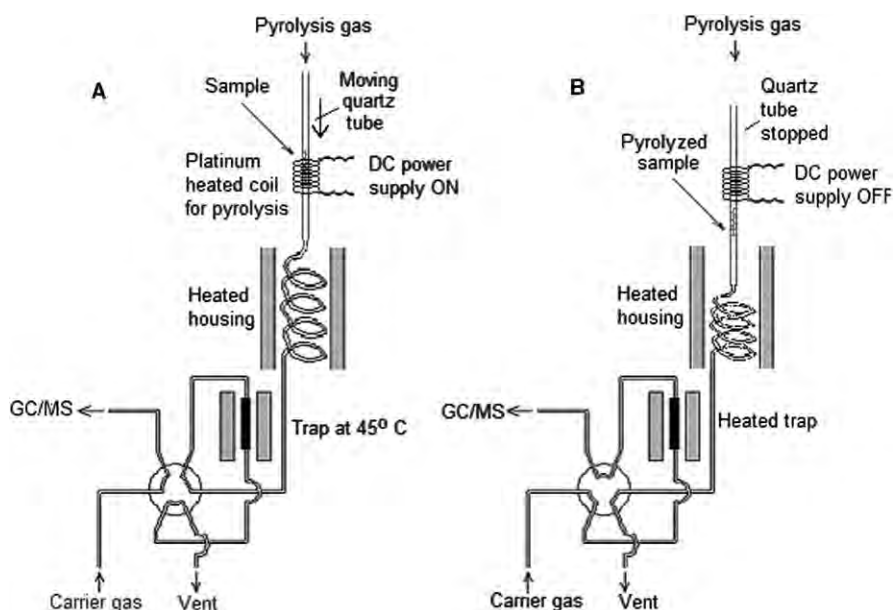


FIGURE 4.4.1. Schematic drawing of the moving heated zone pyrolyzer (based on the design of Pyrobot CDS system). See text for details.

is connected with a GC/MS system that allows detailed analysis of pyrolysis or burning products. The moving heated zone pyrolyzer shown in Figure 4.4.1 allows a change in gases between the one in which pyrolysis is performed and the carrier gas for the GC/MS system. The instrument is equipped with a long quartz tube that contains the sample. The pyrolyzer works in two stages. In stage (A) the tube with the sample is moved at a selected speed through a heated coil reaching the desired pyrolysis temperature. A pyrolysis gas flows through the tube and transfers the pyrolysates to a trap at room temperature. The trap typically contains Tenax, but other sorbent materials can be used. In stage (A) a carrier gas bypasses the trap and flows directly to the GC/MS system. In stage (B) the heating coil of the pyrolyzer is turned off, and the flow of carrier gas is switched through the trap and further into the GC/MS. At the same time, the trap is heated (e.g., at 300 °C) and is desorbed, transferring the pyrolysates into the GC/MS for analysis.

Pyrolysis can be performed on various material weights; at different temperatures (up to 1200 °C), different heating times, different heating rates, different speeds of moving the heated zone (including zero speed), and with different pyrolysis gases. The flow of the pyrolysis gas also can be controlled. If burning is the process to be studied, the heating of the sample is done in an atmosphere with a level of oxygen estimated to be equal to that in the burning zone.

#### 4.5. STANDARDIZATION OF ANALYTICAL PYROLYSIS TECHNIQUES

##### *General aspects*

One considerable limitation of the application of analytical pyrolysis in practice is caused by the variability in results and result interpretation for the same sample in different reported studies. Pyrolysates typically are complex mixtures, and the interpretation of results is not always straightforward. The number of constituents in the pyrolysates is frequently high, and the analysis of all components is practically unachievable. Also, the decision for a quantitative limit below which the presence of a specific component is irrelevant in a pyrolysate is sometimes arbitrary or poorly defined. For these reasons the reported results from different studies using pyrolysis may have differences. An accurate description of the level of detail reported for a study may eliminate part of the perceived



variability in the analytical pyrolysis results. Therefore, a careful evaluation of the experimental conditions and a clear understanding of the goal of each study are necessary when evaluating analytical pyrolysis results.

The variability of the difference between the set temperature of pyrolysis and the true temperature of the sample during pyrolysis frequently has been considered one of the parameters responsible for apparent discrepancy in results. The temperature of the sample during pyrolysis can be standardized between different pyrolyzers using a model compound such as the isoprene/styrene copolymer with the trade name Kraton 1107 [80,81]. The procedure is based on the dependence of the composition of the pyrolysis products on temperature. Kraton 1107 decomposes generating isoprene, dipentene, styrene, dimethylvinylcyclohexene, and other small molecules. The ratio of isoprene to dipentene was found to be proportional with the pyrolysis temperature between 500 °C and 850 °C, with a good correlation coefficient (0.964). Several restrictions were imposed on the pyrolysis, such as a heating rate  $\beta$  higher than 2 °C/ms and THT longer than 500 ms. The calibration with Kraton 1107 was done by performing the pyrolysis in an inductively heated or a resistively heated filament pyrolyzer with the analysis performed using a gas chromatograph. The isoprene/dipentene ratio was obtained from the ratio of the chromatographic peak areas of isoprene and dipentene. The study generated the same results for both heating techniques, the data being shown in Table 4.5.1 [80].

The dependence of  $T$  (°C) as a function of  $r$  = isoprene/dipentene can be given by the expression:

$$T \text{ (°C)} = 527.9 + 68.9r \quad (4.5.1)$$

In principle, equation 4.5.1 allows the calibration of any pyrolyzer for a series of given temperatures with corresponding temperatures acquired by the sample. It is interesting, however, that a study regarding the pyrolysis of Kraton 1107 in a furnace pyrolyzer [36] found linearity between  $T$  and  $r$  only at temperatures between 450 °C and 625 °C.

The variability in the results of pyrolysis studies is caused mainly by the large number of parameters that can be chosen for this technique. Among these parameters are the type of pyrolyzer (filament, Curie point, micro furnace, laser, etc.) and the parameters for the pyrolysis process, such as the (final) equilibrium temperature  $T_{eq}$ , the heating rate TRT, the heating time THT, and the quantity of sample taken for analysis. The nature of the sample also influences the reproducibility of the results. For example, the samples with a relatively low boiling point (such as liquids) or the liquid components from composite samples may evaporate in part (or even completely) before the pyrolyzer attains the  $T_{eq}$ , either due to the relatively high temperature of the pyrolyzer housing ( $T_{hou}$ ) or because the TRT is not short enough. The result is variability in the pyrolysis products in their quantities or even in their nature. Some composite samples that contain volatile components may be analyzed using a step pyrolysis program, where the volatile components are first evaporated at a lower temperature, and then the remaining solid part of the sample is truly pyrolyzed at a higher temperature. Pyrolysis instruments having a headspace option are available for the analysis of this type of sample [28]. For solid samples that decompose easily, the  $T_{hou}$  may induce preliminary decomposition, which depends on the time the sample is kept in the housing before the pyrolysis itself. This time, which is not usually controlled, may generate irreproducibility in the pyrolysis results for samples that easily decompose. The pyrolysis of stable solid samples is less influenced by these parameters.

When GC/MS is used for the analysis of the pyrolysate, the adjustment of the parameters associated with the GC/MS side also lead to variability in the final results. These may include the chromatographic column used for the separation, the GC oven temperature program, the injection port characteristics (temperature, carrier pressure, injection type, etc.), as well as the mass range for the MS analyzer and

TABLE 4.5.1. Isoprene/dipentene ratio as a function of temperature for Kraton pyrolysis

Temperature (°C)	Isoprene/dipentene
650	1.76
700	2.52
750	3.21

the sensitivity of the MS instrument. Changes in any of these parameters may lead to some problems for the reproducibility (between laboratories), although repeatability of results (performed in the same laboratory and with the same equipment) for experiments performed in identical conditions may be very good. This range of potential changes (intentional or unintentional) in the parameters used for analytical pyrolysis limit to a certain extent the utilization of this technique.

#### 4.6. CONDITIONS FOR PYROLYSIS EXPERIMENTS IN THIS BOOK

##### *General aspects*

A variety of PY-GC/MS experimental conditions are reported in the literature. In Part 2 of this book, in addition to the data collected from literature, some original results are reported. These results were obtained using several experimental setups, which are summarized in this section. Three types of pyrolyzers were used, as below.

##### *Type 1 Experiment*

A filament pyrolyzer Pyroprobe 1000 (CDS Analytical, CDS, Oxford, PA 19363, USA) online with a 6890/5973 GC/MS instrument (Agilent, Wilmington, Delaware 19808, USA). This system can be used in flash mode or with a specified temperature increase rate, but with only one value for the final temperature, with pyrolysis performed in the carrier gas (helium), and with no autosampler capability.

##### *Type 2 Experiment*

A filament pyrolyzer Pyroprobe 2000 with an AS 2500 autosampler (CDS Analytical), off-line. This system can be used in flash mode or with a specified temperature increase rate, with up to five temperature steps. The pyrolysate can be analyzed online (Type 2a Experiment), or the pyrolysate can be collected in a cooled capillary (see Section 4.2) and analyzed off-line after dissolution in a solvent or after derivatization (Type 2b Experiment).

##### *Type 3 Experiment*

A filament pyrolyzer Pyroprobe 5000 Series, Model 5200 (CDS Analytical) online with a 6890/5973 GC/MS instrument (Agilent). This instrument can be used in flash mode or with a specified temperature increase rate, several temperature steps, direct transfer of the pyrolysate to the GC/MS system, or with an initial Tenax<sup>®</sup> trap collection followed by the trap desorption. The use of the trap allows the pyrolysis to be performed in a different atmosphere from the carrier gas. This system does not have an autosampler, but it can be connected to a moving heated zone accessory (see Figure 4.4.1).

The GC/MS analysis of the pyrolysates can be done using a variety of conditions that are adjusted to obtain the best results. However, for a better standardization of the pyrolysate analysis, when possible the online analyses were performed using a unique set of GC/MS parameters as described in Table 4.6.1.

The DB-1701 type column (Agilent/J&W Scientific) has medium polarity and separates well low-molecular-weight components of the pyrolysates. However, for compounds with high boiling points, very polar compounds, or compounds that decompose when heated, the separation on this column is not adequate, and another experimental setup for the GC/MS side of the pyrolysis must be selected.

The off-line experiments were usually done when a derivatization of the pyrolysate was necessary in order to analyze very polar compounds. Derivatization also was used when the pyrolysis products were expected to have high boiling points or when traces of a specific compound or group of compounds were analyzed using a dedicated procedure. The pyrolysate was collected in a short uncoated 0.53 mm capillary column that was cooled in iced water. The typical derivatization was trimethylsilylation. For this

TABLE 4.6.1. *Typical parameters for the GC/MS online analysis of pyrolysates*

Parameter	Description
GC column	DB-1701
Column dimensions	60 m long, 0.25 mm i.d.
Film thickness	1.0 $\mu$ m
Initial oven temperature	37 °C
Initial time	4.0 min
Oven ramp rate	2 °C/mm
Oven final first ramp	60 °C
Final time first ramp	0 min
Oven ramp rate	5 °C/mm
Oven final temperature	280 °C
Final time	20 min
Total run time	75.5 min
Inlet temperature	280 °C
Inlet mode	Split
Carrier gas	Helium
Flow mode	Constant flow
Flow rate	1.1 mL/min
Nominal initial pressure	17.5 psi
Split ratio	70:1
Split flow	76.0 mL/min
GC outlet	MSD
Outlet pressure	Vacuum
MSD transfer line temperature	280 °C
Ion source temperature	230 °C
Quadrupole temperature	150 °C
MSD EM offset	250 V
MSD solvent delay	2.0 min
MSD acquisition mode	TIC
Mass range	29–550 a.u.

derivatization, the collected material was treated in the capillary with 0.15 mL of a mixture of one part dimethylformamide (DMF) and two parts bis(trimethylsilyl)-trifluoroacetamide (BSTFA) (see Section 4.2). The samples were transferred into GC vials, kept at 76 °C (in a heating block) for 30 min, and allowed to cool at room temperature for another 30 min. The analyses were done using a 6890/5973 GC/MS instrument (Agilent). The parameters for the GC/MS analysis are given in Table 4.6.2.

Other GC/MS procedures for pyrolysate analysis that were used in special cases are discussed in Part 2 of this book.

Qualitative identifications of the peaks generated in the pyrograms for the original experiments described in this book have been done almost exclusively using mass spectral identifications. The mass spectral libraries used for these identifications included NIST02, NIST08 [82], Wiley275, Wiley7n [83], and PAL600K [84]. Some identifications in the tables were only tentative and were indicated with “?”. Associated with the chemical identifications for many compounds, the CAS Registry Numbers (CAS#) were indicated [85]. The CAS# was not available for some compounds, and this was indicated with “N/A” (not available). Due to the wide use of mass spectra for the analysis of pyrolysates, the MW of compounds in the whole book is given for the most abundant natural isotope and rounded to the unit. For example, MW of decene is given as 140 and not as 140.27.

TABLE 4.6.2. *Typical parameters for the off-line GC/MS analysis after TMS derivatization of pyrolysates*

Parameter	Description
GC column	DB-5MS
Column dimensions	30 m long, 0.25 mm i.d.
Film thickness	0.25 $\mu\text{m}$
Initial oven temperature	50 $^{\circ}\text{C}$
Initial time	0.5 min
Oven ramp rate 1	3 $^{\circ}\text{C}/\text{mm}$
Oven final first ramp	200 $^{\circ}\text{C}$
Final time first ramp	0 min
Oven ramp rate 2	4 $^{\circ}\text{C}/\text{mm}$
Oven final temperature	300 $^{\circ}\text{C}$
Final time second ramp	10 min
Oven ramp rate 3	4 $^{\circ}\text{C}/\text{mm}$
Oven final temperature	300 $^{\circ}\text{C}$
Final time third ramp	10 min
Total run time	101.75 min
Inlet temperature	300 $^{\circ}\text{C}$
Inlet mode	Split
Injection volume	1.0 $\mu\text{L}$
Flow mode	Constant flow
Flow rate	1.0 mL/min
Nominal initial pressure	7.57 psi
Split ratio	30:1
Split flow	28.8 mL/min
GC outlet	MSD
Outlet pressure	Vacuum
MSD transfer line temperature	280 $^{\circ}\text{C}$
Ion source temperature	230 $^{\circ}\text{C}$
Quadrupole temperature	150 $^{\circ}\text{C}$
MSD EM offset	100 V
MSD solvent delay	7.0 min
MSD acquisition mode	TIC
Mass range	29–800 a.u.

The quantitation using pyrolysis can be done following the typical procedures in GC/MS analyses, after generating a calibration curve between the MS response (peak area count) and a specific amount of analyte. However, with complex pyrolysates it is very difficult to generate such calibrations for a large number of compounds. An estimation of the levels of various compounds in the pyrogram can be done by simply comparing the peak area counts of the compound of interest with that of a peak generated by a compound present in a known amount (e.g., a standard that does not decompose by pyrolysis). Another procedure is to make estimations based on areas normalized by the sum of all peak areas in the chromatogram. Since the response (signal/quantity) in GC/MS is not equal for different compounds, these procedures are not a true quantitation. The estimation based on normalized peaks by the total peak areas in the chromatogram and by the molecular weight of the individual compound is used in this book for providing a rough estimation of the moles level of different compounds in the pyrogram. However, it must be noted that these estimations sometimes can be misleading since differences in the response factors in the analytical procedures can be quite large for different compounds.

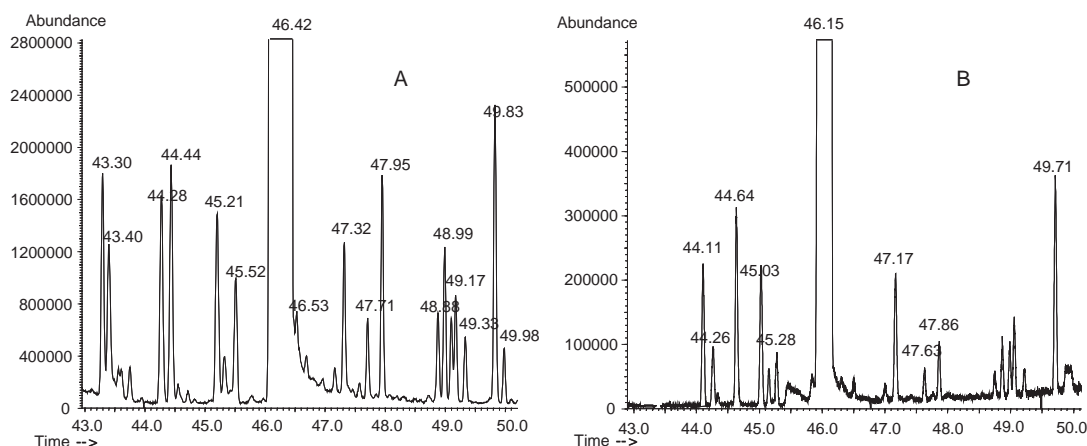


FIGURE 4.6.1. Time window between 43 min and 50 min in the pyrogram of 1-bromodecane (A) and the same time window for the chromatogram of a solution of 1-bromodecane in cyclohexane (B).

Since the purity of the parent compounds used in pyrolysis experiments is not always perfect, some compounds detected in the pyrolysates may come from the impurities in the initial sample and are not a result of the pyrolysis process. Therefore, it is not always possible to know the origin of a pyrolysate component without a preliminary analysis of the initial sample. The samples that were used in pyrolysis experiments and are described in this book were frequently subjected to a GC/MS analysis. For this purpose, solutions of the compound taken for pyrolysis were injected in a GC/MS system working in conditions virtually identical to those described in Table 4.6.1. An example of impurities detected in a parent compound is given below for 1-bromodecane. The pyrolysis of this compound is described in Section 8.2. A time window between 43 min and 50 min in the pyrogram of 1-bromodecane is shown in Figure 4.6.1A. The parent compound elutes at 46.42 min. A number of minor peaks are also seen in the pyrogram. The same time window is shown in Figure 4.6.1B for the chromatogram of a solution of 1-bromodecane in cyclohexane analyzed using identical GC/MS conditions as the pyrolysate. The chromatogram (side B) shows a number of peaks similar to those from the pyrogram (a shift in the retention time for identical compounds is seen between pyrogram A and chromatogram B, caused by the use of different instruments).

The peaks in the pyrogram identical with those in the chromatogram of the solution of 1-bromodecane were not a result of pyrolysis, and the corresponding compounds had to be eliminated from the list of pyrolysis products of 1-bromodecane. Since the rest of the chromatogram was “clean,” no other suspected impurities were present in the parent compound.

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## CHAPTER 5

*Basic Concepts Regarding Risk Assessment and Toxicology***5.1. RISK ASSESSMENT PRINCIPLES*****General aspects***

Risk assessment is the common first step in the risk management process. It determines the quantitative and/or qualitative value of risk [1]. Risk management is the process of defining and implementing measures to control a risk [2]. Risk assessment takes into account factors relevant to the situation assessed, such as the current or proposed human activities, specifics related to exposure to the agent assessed, and, in case of chemical hazard, the agent's physicochemical characteristics. The essential steps involved in risk assessment, beyond the identification of an issue, are (1) hazard identification, (2) dose–response assessment, (3) exposure assessment, and (4) risk characterization. After an issue has been identified, the specific problems are identified, involving information related to the potential causes and context of the problem, the associated types of adverse effects, the frequency and duration of the problem, public perceptions, etc.

The hazard identification step involves evaluating the available data to define the adverse health effects that are related to the problem including frequency and duration of exposure. Dose–response assessment evaluates the qualitative and quantitative toxicity data to estimate the incidence and severity of adverse effects occurring at different exposure levels. Exposure assessment involves devising estimates that take into account potential exposure scenarios, magnitude, duration, length of exposure, and frequency of exposure to a hazard. The risk characterization step details the effects (incidence, nature) for the specific exposure scenarios. Besides capturing all the findings from steps 1, 2, and 3, this step also defines the uncertainties (magnitude, nature) and assumptions used in the risk assessment. Risk management takes into account all the risk assessment findings and considers pertinent external factors before reaching a decision [2].

***Uncertainty and variability in risk assessment***

Uncertainty and variability are usually part of risk assessment. Uncertainty is usually the result of insufficient knowledge (lower data quality, insufficient studies, or lack of studies), the result of parameter uncertainty (e.g., random measurement, systematic errors, multiple uncertainty errors from incorrect or unrealistic model application), and decision-related uncertainty (prediction interpretation inability or limitation). Variability may result from differences in people or populations and can occur when a single value is used to describe something characterized by multiple or variable values (e.g., body weight, other interindividual differences).

Uncertainties in data sets and data gaps are the weak points of risk assessment. One way of dealing with uncertainty relies on incorporation of safety and uncertainty factors when deriving risk levels. This is the route probably used most often, although, within some limits, the specific factors used to select a given uncertainty or safety factor often have an arbitrary basis for being chosen.

***Risk assessment guidance documents***

Different countries have different authoritative bodies that have developed their own set of criteria for risk assessments. For example, there are various approaches for conducting carcinogen assessment [3]. In the United States, the most elaborate current risk assessment guidelines have been produced by the Environmental Protection Agency (EPA). EPA has guidelines for carcinogen risk assessment,



mutagenicity, neurotoxicity, developmental toxicity, reproductive toxicity, chemical mixtures, and ecological risk assessment [4].

## 5.2. TOXICOLOGY PRINCIPLES

### *General aspects*

Toxicology is the study of the adverse effects of substances on organisms, their mechanisms of toxic action, and the application of the collected information to protect the health of human and other species [5].

In order for a toxicant to generate toxic effects on an organism, either the compound by itself or its metabolites or biotransformation products must come in contact with the affected organism via one or more exposure routes [6]. The exposure route refers to the way individuals come in contact with a potentially toxic substance. The main routes of exposure are eating/drinking (ingestion via gastrointestinal tract), breathing (inhalation via respiratory system), or skin contact (dermal).

In terms of duration and frequency of exposure, toxic effects can be divided into acute, subacute, subchronic, and chronic. Acute exposure takes place for a short period of time, such as less than 1 day. Subacute exposure generally occurs for less than 1 month, subchronic exposure generally occurs for less than 3 months (1–3 months), and chronic exposure is generally more than 3 months [2]. The exposure can take place in a single administration or under repeated administration.

Acute toxic effects are often different from chronic toxic effects. Chronic toxic effects occur when the system is repeatedly or continuously exposed to toxic doses that induce irreversible changes at the site of action and/or if there is not enough time for the biological system to repair the damage in the time intervals between repeated exposures. Chronic effects can also occur if accumulation occurs (e.g., if absorption exceeds biotransformation and/or excretion).

### *Dose and response*

The dose can be defined as the amount of chemical to which an organism or a population is exposed. The usual unit of measure for dose is mg/kg body weight/day. The routes of exposure for which dose is measured in these units include oral, intravenous, intramuscular, subcutaneous, and dermal. Sometimes, dose can be given on weight per body surface area basis or mg/cm<sup>2</sup>. Concentration is used when inhalation exposure is involved and is usually expressed in units of mg/m<sup>3</sup> [2].

The response, or the adverse or toxic effect, can be any departure from normality at any level of a biological system. An adverse or toxic effect, for example, can occur at the smaller biological levels (e.g., molecules in DNA), or it can occur at higher biological levels (e.g., cells, organs, systems). Responses or effects can be localized or generalized (systemic), immediate or delayed, reversible or irreversible, and graded or continuous.

Toxic effects or responses can affect one or more particular organ systems. Usually, the type of toxicity is categorized on the basis of the major organ systems affected. Most chemicals generally induce systemic toxic effects in one or two main organs (target organs). However, the target organ is often not the same as the organ with the highest concentration of the chemical.

### *The relation between dose and response*

Almost any agent given in a high enough dose and/or for long enough time can elicit toxicity (dose makes the poison). Typically, as the dose increases, the toxicological response increases. Each chemical has its own specific dose–response curve for a given effect. The dose–response curve is generally sigmoidal. However, for some compounds, the total absence is detrimental, a favorable biological response is shown for a low exposure, and the compounds are toxic at large doses. This effect is known as hormesis, and, in this case, the typical dose vs. response behavior is not followed.

Also, the dose–response relationship does not necessarily hold true if the response is an allergic reaction.

The description of the dose vs. response regarding the toxicity of a specific compound can be done by many procedures. A simple parameter used for the characterization of dose and response relation is the median lethal dose  $LD_{50}$  (lethal dose, 50%), which is the dose of a toxic substance (or radiation) required to kill half of the members of a tested population (usually of rats). The  $LD_{50}$  value is in general used for the description of acute toxicity. It should be noticed that  $LD_{50}$  is not the lethal dose for all the subjects, some subjects being killed by less toxicant and others surviving even higher doses. Also, the method of administration of a toxic compound may influence the  $LD_{50}$  value. To the  $LD_{50}$  value, sometimes is added a specification regarding the timing of lethality (e.g.,  $LD_{50/30}$  indicates 50% lethality after 30 days). A similar descriptor for dose–response relation is  $LCt_{50}$  (lethal concentration and time, 50%). Another parameter is  $ICt_{50}$ , which is the dose that will cause incapacitation rather than death, and it can be applied more easily to humans.

Some toxicity studies generate information known as NOAEL (no observed adverse effect levels), which gives the lowest tested dose of a toxicant below which no response is observed. This dose is typically expressed as a level or concentration, for example, in units parts per million (ppm). In addition to the level, description of the type of animals in which the study has been performed, time of exposure, as well as the system affected (respiratory, hematological, dermal, etc.) are indicated together with the NOAEL value. A similar descriptor to NOAEL is LOAEL (lowest observed adverse effect levels). A more quantitative procedure for dose–response assessment is benchmark dose (BMD) approach (see, e.g., [7]). In this procedure, dose–response curves are typically used for the evaluation of a predetermined dose that results in a certain level of adverse response or critical effect size [8].

All the previously described parameters are based on the assumption that there is a dose below which no toxic effect occurs (i.e., there is a threshold for noticeable toxicity). An exception to this assumption is carcinogenicity, in which case it is generally assumed that there is no threshold. Most current cancer risk assessment approaches assume that there is no threshold below which the risk of an adverse effect occurring is negligible. In cancer risk assessment, extrapolation models either statistical (based on probability distributions) or mechanistic (based on mechanism of response) can be used to generate risk at very low levels. This low risk is called *de minimis* risk, meaning a risk so small that it does not pose concern. This type of small risk usually is assumed to have a probability of occurrence below  $10^{-4}$  to  $10^{-6}$  and can be interpreted as “virtually safe.”

### ***Carcinogenic potency***

A numerical description indicated as  $TD_{50}$  typically has been used to estimate carcinogenic potency. Similar to  $LD_{50}$  and with NAOEL or LAOEL, this parameter is evaluated for specific animals. The parameter is defined as the dose rate in mg/kg body weight/day, which, if administered chronically for the standard life span of the species, will reduce to half the probability for the animals to remain tumorless.  $TD_{50}$  is analogous to  $LD_{50}$ , and a low value of  $TD_{50}$  indicates a potent carcinogen, whereas a high value indicates a weak one.  $TD_{50}$  can be computed for any particular type of neoplasm, for any particular tissue, or for any combination of these. The determination of  $TD_{50}$  values can be further complicated if the measurement experiments are terminated before the standard life span of the tested animals. Various correction procedures were developed for the evaluation of acceptable  $TD_{50}$  values [9,10]. A relative carcinogenic potency can be calculated to compare the carcinogenic potency of specific compounds. This relative potency can be calculated by comparing the values of  $1/TD_{50}$  for the compounds of interest. For the relative potency, the higher numbers indicate a more potent carcinogen.

### ***Classifications of toxicants by various agencies***

There are various agencies in the United States and abroad that have different classification schemes (qualitative descriptors) for the toxic effects of chemicals, and for chemicals that are carcinogens and reproductive toxicants. In the United States, these agencies include National Toxicology Program (NTP), US EPA, American Conference of Governmental Industrial Hygienists (ACGIH), Occupational

TABLE 5.2.1. IARC and EPA (2005) categories of carcinogens [12,13]

IARC			EPA 2005		
Category	Descriptor	Evidence	Category	Descriptor	Evidence
1	Carcinogenic to humans	Sufficient in humans	A	Carcinogenic to humans	Sufficient in humans
2A	Probably carcinogenic to humans	Limited (or occasionally inadequate) in humans Sufficient in animals	B1	Likely to be carcinogenic to humans	Limited in humans Sufficient in animals
2B	Possibly carcinogenic to humans	Limited or inadequate in humans Sufficient in animals (level of evidence 2A > 2B)	B2	Likely to be carcinogenic to humans	Inadequate or no data in humans Sufficient in animals
			C	Suggestive evidence of carcinogenic potential	No data in humans Limited in animals (more data needed)
3	Not classifiable as to its carcinogenicity to humans	Inadequate in humans Inadequate or limited in animals (more data needed)	D	Inadequate information to assess carcinogenic potential	Inadequate human and animal data or no data
4	Probably not carcinogenic to humans	Demonstrated lack of carcinogenicity in animals and humans (or, occasionally, insufficient in humans, sufficient evidence for lack of effects in animals and supporting mechanism)	E	Not likely to be carcinogenic to humans	Evidence of noncarcinogenicity in at least two animal studies in different species or adequate human and animal data

Safety and Health Administration (OSHA), and Office of Environmental Health Hazard Assessment (OEHHA) of the California EPA, which issued what is known as the “Proposition 65 list of chemicals known to the state to cause cancer for purposes of the Safe Drinking Water and Toxic Enforcement Act of 1986” or “Proposition 65” [11]. A number of international agencies also have classifications for known toxicants, carcinogens, and other classes of hazards, one of these being the International Agency for Research on Cancer (IARC).

Although most classifications are similar, each agency classification has specific differences, and the classifications can be based on different criteria. Also, these classifications are evolving, and they may have differences in the guidelines from one year to another. As an example, the differences in the classification of carcinogens by IARC [12] and EPA in 2005 [13] are shown in Table 5.2.1.

### Factors influencing toxicity

Toxicological assessment is a complex process due to the many factors affecting toxicity. Among these factors can be listed: physicochemical properties of the agent (or vehicle), dose, length of exposure, frequency of exposure, route of exposure, absorption, distribution, metabolism, excretion, species,

strain, interindividual susceptibility, preexisting condition of the exposed individual or population, and other coexposures. Other factors include coexposure-related conditions (e.g., temperature, light, food) and biological system-related conditions (e.g., coexistent stress, other environmental conditions, age, health status, hormones, sex). For these reasons, a number of different tests on several animal species are necessary to arrive to an acceptable understanding of the toxicological profile of a given compound.

One other aspect that must be considered in toxicity assessment includes possible interactions of chemicals. This may occur when more than one chemical is present in a given system and the response can be modified by potentiation, additivity, synergy, or antagonism. Chemicals can interfere by altering each other's absorption, metabolism, distribution, excretion, or protein binding, directly or indirectly.

Tolerance is another effect that must be considered. Tolerance can be seen in situations in which a chemical (or structurally related compound) is administered repeatedly, and it involves decreased responsiveness of a system (e.g., organ, tissue, or cell) to the toxic effects of that chemical. Tolerance depends on the chemical characteristics, individual characteristics, and administration conditions.

### ***Information used in toxicological evaluations***

Toxicological evaluations usually include two main types of information: (1) chemical related and (2) effect/mechanism related. The main sources for toxicological information are in vivo studies (in living organisms), in vitro studies (outside of living organisms, in isolated systems), and in silico data (computer simulation). Studies in vivo can be performed in humans, in animals, or in other living organisms. Studies in humans typically include epidemiological studies and controlled clinical studies. Epidemiology studies are studies on human populations that attempt to link human health effects to a cause (e.g., cancer linked to exposure to a specific chemical, such as asbestos). Clinical studies usually involve studies conducted as part of the safety assessment of medications or devices. Studies in animals include studies in various species and conditions. In vitro studies usually involve studies in bacteria or mammalian cells and are generally used as supporting studies to the interpretation of the in vivo studies. In silico data involve understanding structure–activity relationships (quantitative or qualitative). These are also used as supporting information that is taken into account in an assessment.

### ***The use of toxicological information for risk assessment***

The descriptors used to assess the dose–response relation are further used in risk assessment with the goal to generate parameters that can be applied to estimate admissible levels of exposure to toxicants or drugs, levels that are considered protective of the public health. Such parameters include reference dose (RfD), reference concentration (RfC), and acceptable daily intake (ADI). These parameters usually are generated from NOAEL, LOAEL, or BMD values by applying correction factors such as safety factors (SF), uncertainty factors (UF), and/or modifying factors (MF) [14]. As an example, the ADI is defined as the amount of chemical to which a person can be exposed daily over extended time (usually lifetime) with minimal risk of adverse effects. There are different formulas for the calculation of ADI. One calculation uses the NOAEL and SF values:

$$ADI = \frac{NOAEL}{SF} \quad (5.2.1)$$

Other calculations generate an ADI<sub>1</sub> value by the formula:

$$ADI_1 = \frac{NOAEL}{UF \times MF} \quad (5.2.2)$$

The use of LOAEL instead of NOAEL is used for the calculation of an ADI<sub>2</sub> value:

$$ADI_2 = \frac{LOAEL}{UF \times MF} \quad (5.2.3)$$

The safety factor, SF, is selected based on an estimated extreme worst case or can be generated as  $UF \times MF$ , where the uncertainty factor, UF, accounts for different types of extrapolations or compensations depending on the source of NOAEL and LOAEL values (e.g., NOAEL generated from animal studies, or using adult–child extrapolation, etc.), and where the MF values are adjusting factors for UF.

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## CHAPTER 6

*The Utility of Pyrolysis Studies***6.1. INFORMATION FROM ANALYTICAL PYROLYSIS*****General aspects***

Analytical pyrolysis has a number of characteristics that can make it a very powerful investigative tool. The technique usually requires a small amount of sample and can be set with very low limits of detection for a number of analytes. For Py-GC/MS, the identification capability of volatile pyrolysate components is exceptionally good. A range of information can be obtained using this technique, including identification of compounds in pyrolysates that are potentially harmful. In most cases, the analysis does not require any sample preparation, not even solubilization of the sample, which may be a difficult task for some types of materials. The analysis can be automated easily, and the instrumentation for the pyrolysis itself is not expensive and can be connected easily to the existent analytical instrumentation in a laboratory (such as a GC or a GC/MS instrument).

Analytical pyrolysis, typically having a GC/MS as an analytical instrument (Py-GC/MS), can provide both qualitative and quantitative information regarding pyrolysates. One common purpose for this technique is to determine the nature of the material that was pyrolyzed [1]. This is possible either through use of the composition of the pyrolysate (obtained by an analytical technique such as GC/MS) as a “fingerprint” of the parent molecule, or from the similarity of the structure of fragment molecules from the pyrolysate with that of the parent compound. Although this utilization is less common for non-polymeric molecules, it still has its potential for small molecules, and is applied mainly for compounds that have volatility and solubility problems. Analytical pyrolysis applied to non-polymeric materials remains a very useful technique for the understanding of pyrolysate composition applied to compounds generated in human activities such as waste incineration, burning of specific fuels, cigarette smoking, or even burning of food during cooking.

***Qualitative analysis of pyrolysates***

Qualitative analysis in Py-GC/MS is based on the identification of various peaks in the pyrogram, usually with the help of the search capability of mass spectrometer software and the mass spectral libraries (see Section 4.2). The analysis can be limited to the identification of the main components in the pyrolysate, or it may include minor components and sometimes trace components. An example is given below for the pyrolysis of menthol at 800 °C in helium for 10 s. The separation was performed on a DB-1701 GC column (Agilent/J&W Scientific, Wilmington, DE), 60 m long, 0.25 mm i.d. with 1 µm film, in gradient conditions between 37 °C and 260 °C. The same pyrogram is shown at two different scales for the peak abundance. The differences in the details are obvious when the pyrograms shown in Figures 6.1.1 and 6.1.2 are compared. The first figure displays only the major peaks and the second includes minor peaks for the same pyrolysate.

In Figure 6.1.1 only menthol and 3-menthene are shown. Figure 6.1.2 shows minor components from the same pyrolysate, which are listed in Table 6.1.1, as obtained using a mass spectral library search.

A number of very small peaks were not identified in the chromatogram of Figure 6.1.2. It is common that some compounds are present at trace levels in pyrolysates and can be below the limit of detection of the analytical instrument (e.g., a GC/MS). The presence of trace compounds can be verified only by using larger amounts of pyrolysate than those typically generated in analytical pyrolysis, and in these situations dedicated methods of analysis using cleanup and concentration steps for the analysis are necessary.

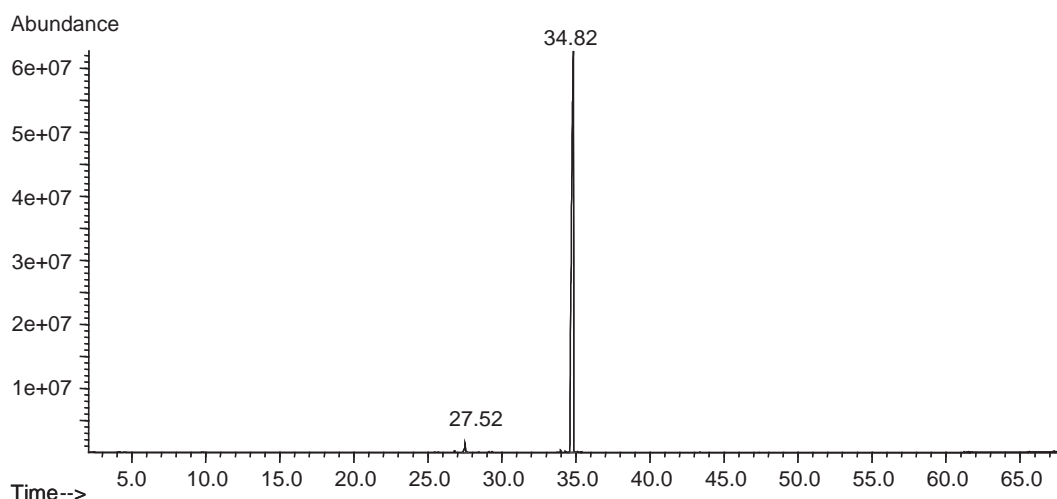


FIGURE 6.1.1. Pyrogram of 1.0 mg menthol at 800°C in He for 10 s showing the peak for menthol at 34.82 min and the peak for 3-menthene at 27.52 min.

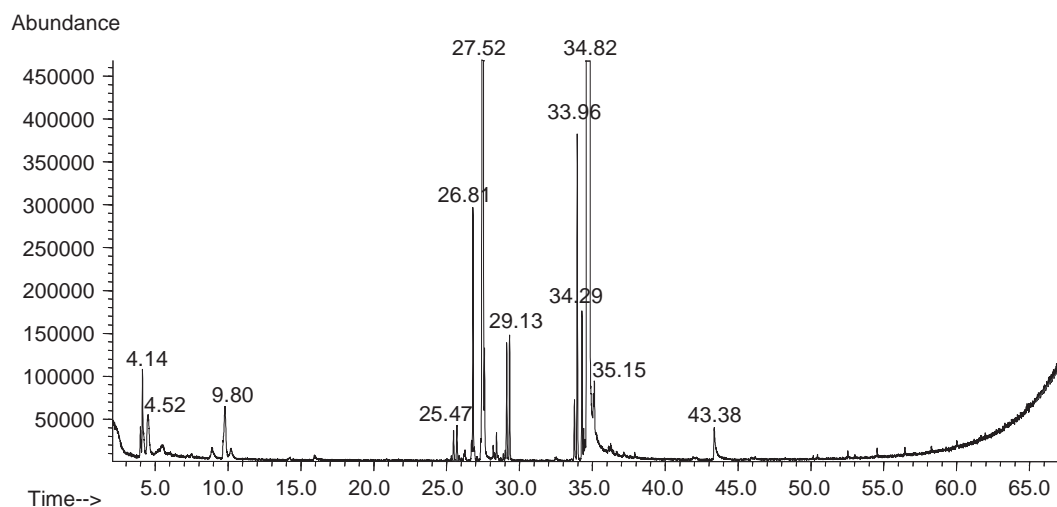


FIGURE 6.1.2. The same pyrogram as shown in Figure 6.1.1 of 1.0 mg menthol at 800°C in He for 10 s, shown at a different abundance scale.

### Quantitation using Py-GC/MS

Although less common than qualitative analysis, Py-GC/MS can be applied for quantitative purposes. Quantitative analysis is applied more frequently in polymer analysis, for example, in the determination of the amount of a specific polymer in a given complex matrix, such as a composite material, inorganic matrix, etc. However, the quantitative measurement of a pyrolysis product can be used successfully even for the analysis of other organic molecules. Calibration is typically necessary in these situations, and similarly to other analytical procedures, this can be achieved using internal standards, external standards, or a standard addition procedure (e.g., [2]).



TABLE 6.1.1. Compounds tentatively identified in the pyrogram (in the order of retention times) shown in Figure 6.1.2 for menthol, performed at 800°C in helium

Peak no.	Compound	MW	CAS no.	Ret. time	Relative %
1	Cyclopropane	42	75-19-4	4.14	0.08
2	Methylenecyclopropane	54	6142-73-0	4.52	0.08
3	Benzene	78	71-43-2	9.80	0.09
4	1,3-Cyclohexadiene	80	592-57-4	10.21	0.00
5	2,4-Nonadienal	138	5910-87-2	25.47	0.02
6	Cyclohexene, 3-(2-methylpropyl)-	138	4104-56-7	25.70	0.02
7	Cyclopentane, 1-methyl-3-(2-methyl-2-propenyl)-	138	75873-00-6	26.81	0.15
8	3-Menthene	138	N/A	27.52	1.11
9	Cyclohexane, 3-methyl-6-(1-methylethyl)-	138	5256-65-7	27.61	0.07
10	Cyclohexane, 1-methyl-4-(1-methylethenyl)-	138	1879-07-8	28.44	0.02
11	Cyclohexene, 1-methyl-4-(methylethyl)-	138	5502-88-5	29.13	0.07
12	Cyclohexane, 1-methyl-4-(1-methylethylidene)-	138	1124-27-2	29.33	0.07
13	Cyclohexanemethanol, $\alpha$ -propyl-	156	4352-42-5	33.77	0.04
14	Cyclohexanone, 5-methyl-2-(1-methylethyl)-, <i>cis</i>	154	491-07-6	33.96	0.18
15	Cyclohexanone, 5-methyl-2-(1-methylethyl)-, <i>trans</i> (menthone)	154	89-80-5	34.29	0.08
16	Isomenthol	156	N/A	34.41	0.02
17	Menthol	156	1490-04-6	34.82	97.76
18	Cyclohexanol, 2-methyl-5-(1-methylethyl)-	156	499-69-4	35.09	0.04
19	Cyclohexanol, 1-methyl-4-(1-methylethyl)-	156	21129-27-1	35.15	0.09

In Py-GC/MS, the quantitative comparison of the level of different constituents in a pyrolysate is more commonly of interest than the quantitation of a unique compound. However, quantitative evaluation of specific compounds can be important in cases where the compounds generated by pyrolysis pose environmental or health issues, for example, when polycyclic aromatic hydrocarbons (PAHs), aromatic amines, heterocyclic amines, or other compounds of concern are formed. When a substance is generated by pyrolysis and contributes to a specific flavor, such as in burned incenses, cigarette smoke, or broiled/fried food, it is sometimes necessary to measure its amount in a mixture of pyrolysate components.

In order to have reliable quantitative results by Py-GC or Py-GC/MS, an important requirement is the repeatability of the analysis. Any variation of the parameters of the Py-GC/MS analysis may influence the outcome. For this reason, the quantitation using Py-GC/MS is more difficult than that in typical chromatography. The variability is a result of the fact that certain steps in the pyrolytic process may not be perfectly reproducible. Reproducibility is affected mainly when the same sample is analyzed with different types of instrumentation. However, for the same instrument and the same amount of sample, the reproducibility can be very good [3]. Among the procedures used to eliminate the variability in quantitative work using Py-GC/MS are the use of small sample size and the use of instruments with the temperature profile well calibrated. The analysis of a standard substance at specified intervals of time (or number of samples) helps to verify reproducibility and allows the evaluation of the factors that may influence variability. The elimination of these factors may improve the results. One other procedure to improve reproducibility is the use of an internal standard during pyrolysis. However, the addition of a standard is not always simple when the sample weight is below 1 mg and the standard must represent only a small part of the sample. A solution to this problem is to pyrolyze a measured amount of standard diluted in a solid inert carrier, simultaneously with the sample. An example of a solid carrier is crushed silica wool, on which 1%, by weight, of 1,4-dibromobenzene is present as internal standard [4]. The use of solid supports in pyrolysis must be approached with care since they may act as solid catalysts (e.g., active alumina) and change the outcome of pyrolysis.



### Mass balance in analytical pyrolysis

The measurement of the proportion of a specific compound formed in a pyrolysate related to the initial mass of material taken for pyrolysis is a subject of interest for many practical purposes (e.g., [5]). However, this operation is relatively difficult to achieve, since an unknown amount of product generated by pyrolysis is purged from the injection port of the GC and it is not transferred into the chromatographic column of the GC/MS instrument. Also, the whole set of constituents of the pyrolysate is not always amenable for gas chromatographic analysis. This is the case when the pyrolysate contains char, water, carbon dioxide, and nonvolatile components. For these cases the assumption that all pyrolysis products of the initial material are represented in the chromatogram of the pyrolysate (pyrogram) leads to erroneous results. When the pyrolysis results must be reported to the initial amount of sample, either the variation in weight of the initial sample or the quantitation of each component in the pyrolysate (including char) is necessary. A composition of a hypothetical pyrolysate in terms of volatility and suitability to be analyzed by GC (or GC/MS) is shown in Figure 6.1.3. Some materials may generate only volatile compounds that can be completely analyzed with GC/MS instrumentation. Others may generate very few volatile compounds in the pyrolysate.

A relatively cumbersome procedure may generate a true quantitation for a compound in a pyrolysate (assuming that the product is volatile and can be analyzed by a GC/MS method). This consists of performing the calibration by using the housing of the pyrolyzer as the place for injecting the standards of the compound of interest. Even in this case, it must be ensured that the differences in the temperatures of injection in the housing of the pyrolyzer and that of the pyrolyzer heating element does not introduce variations in the injected amount of calibrant.

The results of a quantitation can be presented by reporting them to the total fraction of volatiles that are seen in the chromatogram. This is a simpler alternative, but it gives only a relative comparison of the yields of different volatile compounds from the whole pyrolysate. The normalization of each peak area in a pyrogram by the sum of all peak areas is a good procedure for identifying which compound is generated at a higher yield compared to the other volatiles. However, a normalized peak area does not necessarily represent the true yield of a volatile compound. The detector response for each compound is generally different, and two compounds showing the same peak area in a chromatogram are not necessarily present in equal quantities. Computer programs known as target compound software are available to assist in quantitative analysis, combining the stability of retention times in a given separation with the identification of specific compounds based on several characteristic mass ions. These software packages have the general purpose of quantitation of specific compounds in GC/MS chromatograms and can be applied to Py-GC/MS results. Because of the problems encountered in quantitative Py-GC/MS, its use is typically limited to comparisons and overall characterizations together with qualitative analysis.

Accounting for mass balance of pyrolysis products is a relatively complex task. It depends on the nature of the pyrolyzed material, the pyrolysis conditions, and the analytical procedure for the determination of pyrolysate composition. In some situations, typically when all the pyrolysis products are volatile and detected by the mass spectrometer, the mass balance can be achieved with acceptable

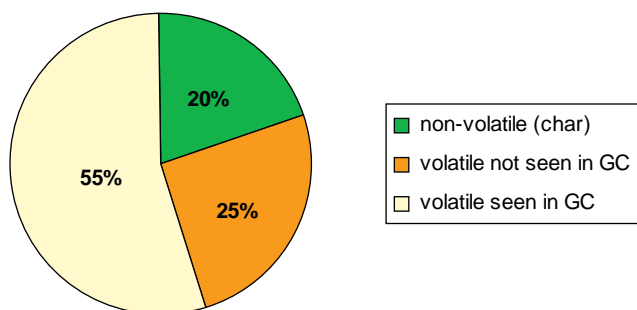


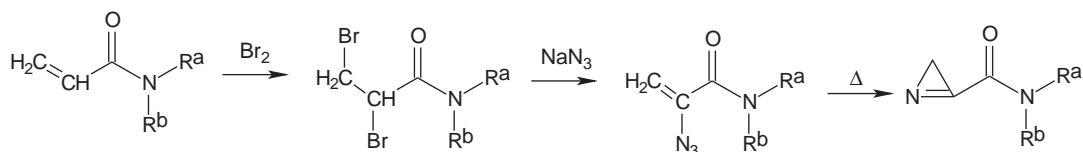
FIGURE 6.1.3. Hypothetic pyrolysate composition in terms of volatility and capability of the pyrolysate to be analyzed by GC (or GC/MS).

accuracy, while in other situations it may be a difficult process that can be accompanied by significant errors. Since the response factors in GC/MS are not all equal, the quantitation based solely on peak areas may not be accurate when a calibration is performed with a different compound. The response factors can be assumed as equal for different compounds only with approximation, and this can be done only for compounds with similar structures. The nonvolatile compounds including the char (which is commonly formed during many pyrolytic processes) and compounds that are not eluted from the chromatographic column must be accounted for when the mass balance is attempted. The choice of a specific type of chromatographic column for the pyrolysate separation is also important in this respect. The possible discrimination of pyrolysate compounds based on volatility that occurs within the injection port of the gas chromatograph must be considered, as well, mainly when the compounds are not formed instantaneously by pyrolysis (slow heating pyrolysis compared to flash pyrolysis). The pyrolysate components that are volatile, but depending on the MS settings may not be detected, including water, CO, and H<sub>2</sub>, should be taken into consideration for a correct mass balance. Water (MW = 18), in particular, is frequently neglected as a pyrolysis product, and is not seen in the pyrograms when the MS mass range is set at higher values (typically above 32 for avoiding any air peak). The presence of traces of air in the atmosphere of pyrolysis, air that is further seen in the program, also may affect the attempts to obtain a mass balance for the pyrolysis products. Typically, the mass balance can be achieved for low molecular weight compounds with high volatility, while it is more difficult to obtain for compounds with higher molecular weight and lower volatility.

## 6.2. THE USE OF PYROLYSIS IN ORGANIC SYNTHESIS

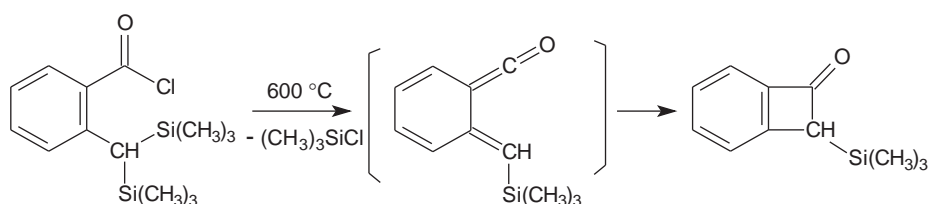
### *Laboratory applications of pyrolysis in organic synthesis*

A large variety of compounds can be obtained using pyrolytic techniques (e.g., [6–17]). The increased temperature promotes reactions that do not occur in other conditions, and unusual compounds can be generated this way. For example, pyrolytic reactions have been used successfully to obtain transient compounds such as benzocyclobutadiene [18] or reactive molecules such as 1-methylpentalene [19]. However, the synthesis of these types of compounds has more of a theoretical interest rather than a practical one. On the other hand, pyrolytic synthesis was proven very useful in some cases for preparation of reactive intermediates necessary in other syntheses. As an example, the preparation of compounds such as 2H-azirine-3-carboxamides can be achieved starting with a substituted amide of acrylic acid in the following chain of reactions [20]:

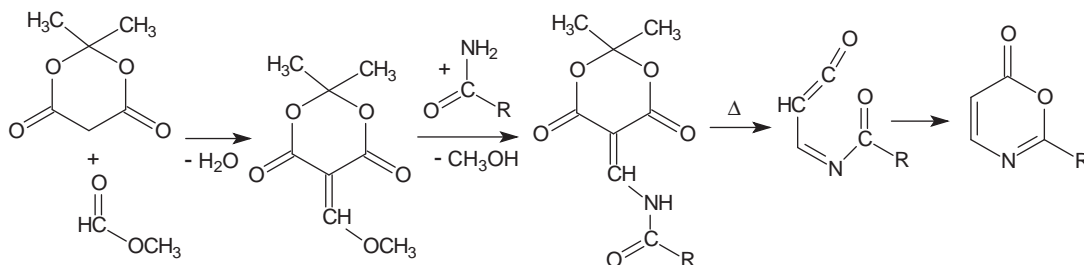


The resulting azirines can be used in Diels–Alder condensations with dienes such as substituted cyclopentadienes or butadienes to form specific heterocyclic compounds.

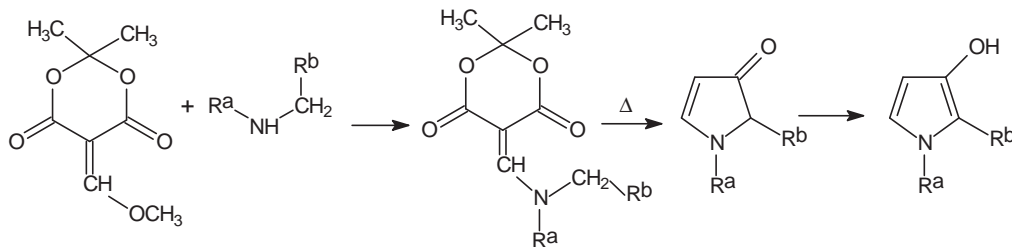
Among other reactive compounds prepared using pyrolysis are, for example, derivatives of bicyclo[4.2.0]octa-1,3,5-triene (benzocyclobutane), which can be obtained as shown below for 2-trimethylsilylbenzocyclobuten-1(2H)-one:



Pyrolytic synthesis also is useful for the preparation of certain stable compounds. A versatile procedure for the preparation of certain heterocyclic compounds uses Meldrum acid derivatives. One such procedure starts with methoxymethylene Meldrum's acid (obtained from Meldrum's acid and methylformate in a Knoevenagel condensation) followed by a condensation with an amide, amine, substituted hydrazine, etc. The resulting compounds can be pyrolyzed to generate the desired heterocycles. Preparation of 1,3-oxazin-6-ones, for example, is achieved by the sequence of reactions shown below [21]:

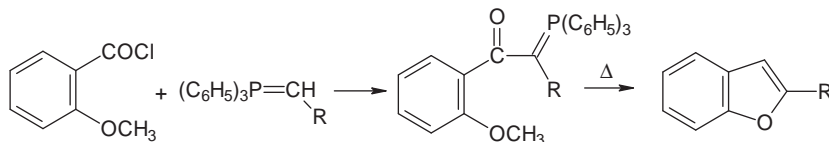


Secondary amines, in a similar chain of reactions, lead to substituted 3-hydroxypyrroles as shown below [22,23]:

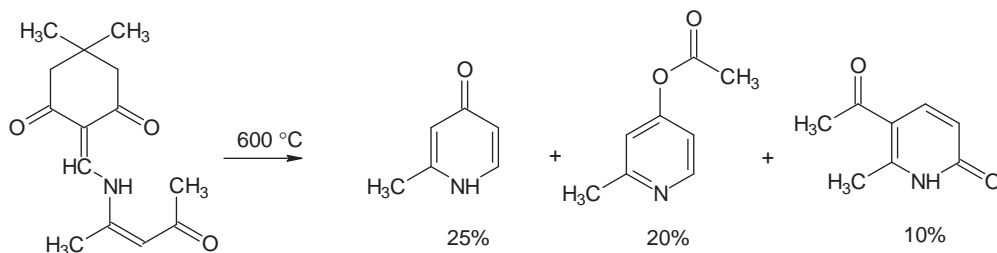


These compounds are of considerable interest, for example, for the synthesis of new antibiotics and immunosuppressants [24]. As an example, pyrolytic synthesis was used for the synthesis of pentenomycin I (see also Section 2.3).

Among other heterocycles, benzofurans can be generated by pyrolytic synthesis. Starting with 2-methoxybenzoyl chloride in a Wittig reaction with an appropriate phosphonium ylide and subjecting the resulting compound to pyrolysis, a substituted benzofuran is generated as shown below [25]:



Simpler molecules also can be obtained using pyrolytic processes. For example, hydroxymethylfurfural can be obtained by pyrolysis from glucose. However, the success of pyrolytic synthetic procedures has limitations. Some of pyrolytic reactions are difficult to use in successful synthetic procedures since mixtures of products and poor yields of the desired compounds are obtained (see, e.g., [26,27]). For example, the pyrolysis of the Meldrum's derivative shown below leads to various compounds:



The separation of the components from the mixture is frequently a difficult task, and other synthesis routes are considered in these cases.

A more recent application of pyrosynthesis is the preparation of carbon nanotubes using spray pyrolysis. The process uses a hydrocarbon, such as benzene, toluene, xylene, cyclohexane, *n*-hexane, *n*-heptane, or *n*-octane, having dissolved a metallocene, such as ferrocene, cobaltocene, or nickelocene, which acts as a catalyst for the nanotube formation [28]. The spray pyrolysis process conducted at 800 °C using, for example, xylene required a concentration of 3% ferrocene for the highest yield of nanotubes. The spray pyrolysis process was performed by spraying the organic solvent solution at a flow rate of 1 mL/min in a flow of argon as a carrier gas at 500 L/h, through a 200-mm-long furnace. Besides hydrocarbons, other compounds can be used for nanotube formation, such as cyclohexanone, diethyl ether, etc.

### Industrial applications of pyrolysis in organic synthesis

Industrial pyrolysis is a part of several of the most important industrial activities including the processing of oil, natural gas, coal, and different types of waste. Considering the production of ethylene alone, which is obtained basically by pyrolytic procedures, the world production in 2003 was  $96.8 \times 10^6$  tons [29]. This ethylene is obtained by pyrolysis mainly from naphtha (a liquid intermediate refining product of crude oil), ethane, or propane, and the proportion of utilization of these sources is shown in Figure 6.2.1. In North America the main source of ethylene is ethane.

Besides ethylene, which is the most important compound generated by pyrolysis, other olefins of industrial importance are obtained by pyrolytic procedures. The list of compounds includes among other compounds propylene, butylene, 1,3-butadiene, acetylene, and some cycloolefins. Pyrolytic processes are also used for the production of aromatic hydrocarbons, such as benzene, toluene, and naphthalene, from heavier naphtha feed or even from crude oil. Catalytic hydrogenation or dehydrogenation associated with pyrolysis is a common operation for the production of hydrocarbons by pyrolysis from naphtha or other sources. The addition of hydrogen in the presence of catalysts enhances the yield of C<sub>7</sub>–C<sub>9</sub> hydrocarbons from the heavier oils, while the pyrolytic dehydrogenation of cycloalkanes in the presence of catalysts leads to the formation of benzene, toluene, and xylenes. Pyrolytic techniques in the presence of catalysts are also used for the purpose of hydrocarbon isomerization, which can generate gasoline with higher octane number. Pyrolysis in the presence of steam and catalysts is used in the oil industry for modifying the chemical composition of different oil fractions. Such important activities at industrial scale are always associated with a large body of studies and published results (e.g., [30–41]). The processing of various resources with the purpose of industrial production of fuels is a very broad subject, with enormous economical implications, and with a large number of studies

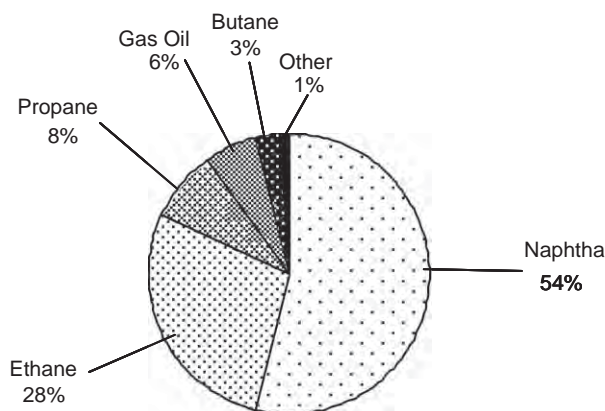
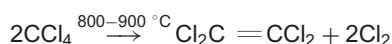


FIGURE 6.2.1. Types of feedstock for ethylene production by industrial pyrolysis (world production [29]).

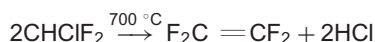
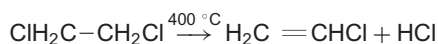
published in books and dedicated journals (*Fuel*; *Fuel Processing Technology*; *Energy*; *Energy Sources*; *Petroleum Science and Technology*; etc.). Many technical details regarding these subjects are beyond the purpose of the present book and therefore not included (see also [42,43]).

One additional field where pyrolysis techniques are used successfully is the industrial production of fuels from renewable sources such as vegetable oils [44–46]. For example, biodiesel fuels obtained from plant triglycerides (e.g., corn, peanut, and sunflower) can be obtained by different pyrolytic processes. Besides being derived from renewable sources, the biodiesel has the advantage that it emits lower levels of pollutants than the regular diesel fuels, and is easier to store, transport, and handle [47]. The viscosity of the initial vegetable oil is reduced following a pyrolysis process [48] due to the fragmentation of the molecules with long carbon chain typically present in vegetable oils.

Other compounds besides hydrocarbons are generated at industrial scale using pyrolysis techniques. For example, tetrachloroethylene, which is used as an important industrial solvent, is obtained at industrial scale by the pyrolysis of carbon tetrachloride using the following reaction:



Other chlorinated or fluorinated compounds, some used as monomers for the preparation of important polymeric materials, can be obtained by pyrolysis, as shown in the following reactions for vinyl chloride and tetrafluoroethylene:



The subject of pyrolysis of different classes of compounds presented in Part 2 includes aspects regarding the chemistry and mechanisms of pyrolysis of compounds involved in these important practical applications. Many aspects regarding pyrolysis of coal, peat, and solid waste (including wood waste, used tires, waste from agricultural products, and municipal solid waste) were not included in this book, since they are more closely related to the pyrolysis of polymers (see, e.g., [49]).

### 6.3. INDUSTRIAL AND LABORATORY APPLICATIONS OF PYROLYSIS IN VARIOUS PROCESSES RELATED TO BURNING

#### *General aspects*

Burning is a very common process, which may take place intentionally, for example, to generate energy or to destroy waste, or may occur unintentionally, as in accidental fires. Besides the combustion process, which is the reaction between a carburant (fuel) and a comburant (oxidant) such as oxygen, some substances involved in the burning process undergo pyrolysis (i.e., decomposition under the influence of elevated temperatures) and not combustion. Pyrolysis, in particular, can generate a wide variety of compounds, many of them undesirable to health and environment. In addition to that, combustion is a highly exothermic reaction, while pyrolysis may generate only very little heat (see Section 3.1). For these reasons, in most burning processes performed intentionally (burning of fuels, burning with the purpose to destroy waste), it is common to attempt to perform as much combustion and as little pyrolysis as possible. Being extremely common for the generation of energy, fuel burning is the subject of numerous studies and of a large number of publications, including books and entirely dedicated journals (*Journal of Fire Science*; *Fuel*; *Combustion and Flame*; *Energy & Fuels*; *Combustion, Explosion, and Shock Waves*; etc.).

Industrial incineration of waste is a very important activity. Pyrolysis studies related to burning are performed in fields such as fuel burning, forest fires, incineration of various types of waste, and formation of dangerous compounds during food processing by heat. These studies can provide information for two different subjects regarding burning: the first is related to the extent of different component processes of burning (pyrolysis, evaporation, combustion, etc.), and the second is related to

the evaluation of the nature of the products that can be generated during burning [50]. Many pyrolysis studies related to burning are focused on the evaluation of the nature of the pyrolysis products. This type of data can then be used in safety assessments to identify any compounds of toxicological concern.

Pyrolysis instrumentation can be used to simulate not only pyrolysis (e.g., by using an inert atmosphere) but also other aspects of burning, such as the generation of vapors and aerosols. Pyrolysis instrumentation also can be used to simulate combustion, by addition of an oxidant (such as air or a specified content of oxygen in an inert gas) during the heating of the sample.

### ***Pyrolysis studies related to fuel burning***

Combustion is typically the main process during the burning of fuels, since the purpose is the generation of energy. Besides many physical aspects of combustion, the chemistry of the process is also important. Combustion by itself may generate undesirable compounds such as CO<sub>2</sub>, CO, and small amounts of N<sub>2</sub>O, NO, N<sub>2</sub>O<sub>3</sub>, NO<sub>2</sub> (designated as NO<sub>x</sub>). Depending on whether or not the burning material contains other elements besides carbon and hydrogen, it can generate larger amounts of NO<sub>x</sub>, SO<sub>2</sub>, COS, CS<sub>2</sub>, as well as other gaseous oxides. The main vapor product of burning is usually H<sub>2</sub>O, but other vapor compounds may be released.

The study of combustion products is a very important subject due to its implications in environmental issues. The efficiency of burning also can be better understood from the composition of the products generated during fuel combustion. Incomplete burning, in particular, is typically associated with the formation of considerable quantities of pyrolysis products and low energy yields.

Combustion gases are of considerable concern regarding environmental problems mainly because of their nature and large quantities. In addition, the pyrolysis component of burning can produce highly toxic and carcinogenic substances. For this reason, the minimization of pyrolysis during fuel burning is usually highly desirable. The formation of pyrolysis compounds depends on the burning conditions and the nature of the fuel that burns. Pyrolytic processes that occur during burning in specific conditions and for various fuels have been extensively investigated and include studies on gaseous fuels [51,52], liquid or solid fuels [42,53,54], vegetable oils [46], and coal [55].

There is a lot of interest in the generation of particular classes of compounds during pyrolysis. Incomplete burning, mainly in automobile engines, emits a variety of hydrocarbons. Although saturated and unsaturated hydrocarbons are emitted at relatively high levels because of incomplete burning, one class of significant interest among the hydrocarbons formed during fuel burning is that of PAHs [53,56–60], which are generated by pyrolytic mechanisms. These substances are of considerable concern mainly because of their carcinogenic properties. Also, certain physico-chemical properties of PAHs that elicit environmental concerns are their hydrophobicity, stability, and persistence, and, therefore, their high residence time in the environment. These properties lead to their accumulation in soil, resulting in the loss of normal soil properties, which affects, in turn, the organisms dwelling in the polluted environment. Another undesirable characteristic of PAHs is their ability to be transported over long distances, which further adds to the complexities of various environmental issues.

In addition to PAHs, another group of compounds that is generated during fuel burning is that of nitro-PAHs [61,62]. The interest in this group of compounds is also related to its toxicological (including carcinogenic) effects and capability to contaminate the environment. Other toxic/carcinogenic substances were identified and studied in fuel exhaust, including, for example, heterocyclic amines [63,64]. A discussion on toxicological properties of these substances from pyrolysates is given in Part 3 of this book.

### ***Pyrolysis studies related to industrial burning of other materials***

Besides fuel burning that is performed for the generation of energy, burning occurs in many other natural (e.g., forest fires) or anthropogenic places (e.g., industrial operations, burning of contaminated sites, municipal waste incinerators, other types of incinerators, and various household activities). Numerous studies are related to the burning of biomass [65–67], wood [68,69], synthetic polymers [70],



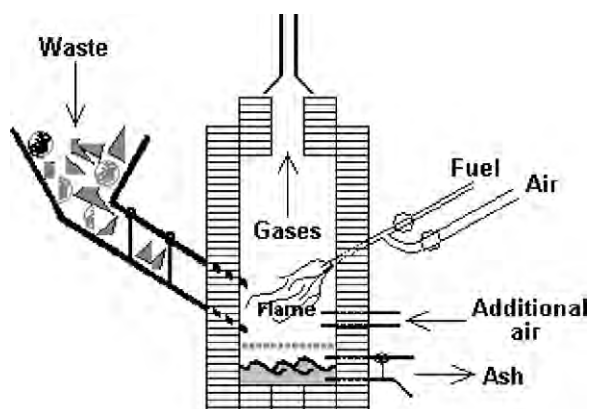


FIGURE 6.3.1. Schematic drawing of an incineration furnace.

used automobile tires [49], and other composite samples containing both polymeric and non-polymeric molecules [71]. Some studies, however, are directed toward entirely non-polymeric materials [72].

Among the many activities related to burning, incineration of waste is of considerable concern regarding environmental pollution, mainly because of the nature and the large quantities of pollutants resulting from this activity. The emissions from incinerators can lead to environmental contamination and occupational problems for the workers in the incinerator facilities. These types of problems lead to regulatory agency restrictions, response from industry, and research to address the problems.

Simple incinerators consist of a furnace adapted with a burner, a source of additional air, and a waste feed. The furnace allows the removal of a large amount of ash and allows an exit for the burned gases. A schematic drawing of such furnace is shown in Figure 6.3.1. The gases from this type of burner may contain undesirable compounds, including solid particles. Various modifications of the simple system are made to improve the furnace performance [73]. For example, afterburners and scrubbers are added to process the exiting gases. The ashes may contain pollutants, and the disposal of these ashes can require specific precautions. The absence of organic matter and carbon from the ash is, for example, an important goal that should be achieved in the process of waste destruction. However, the color of the ash is sometimes the only control on this requirement (white ash vs. black ash).

An important parameter of the incinerator is the temperature achieved in the burning zone. Higher temperatures (as generated, e.g., by plasma pyrolysis technology [74]) may lead to a more complete destruction of the waste material, but may generate higher levels of undesirable substances such as PAHs or other compounds that are stable at higher temperatures. Pyrolysis studies may be necessary for optimization of incineration conditions.

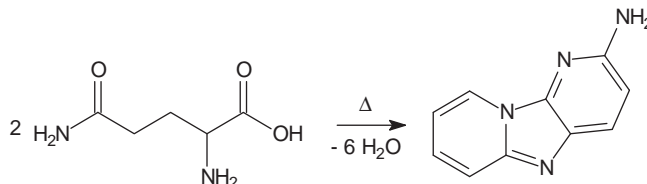
The nature of the materials that are incinerated may be extremely diverse, including polymers and non-polymeric molecules, and may have an organic and/or inorganic nature. The waste can be collected from industrial or agricultural sources, or it may include city waste, medical waste [73], etc. Besides the efficiency in removing the waste, there are numerous other problems related to the use of incinerators, such as their energy efficiency and potential recycling of the output (ashes or even gases).

Pyrolysis studies offer information on the characterization of the pyrolysate profile as well as other burning characteristics. Analysis of pyrolysate compositions is always important in relation to health issues and environmental problems with specific interest in some classes of compounds [75–79]. Among these classes are, again, the PAHs that are generated from various sources [67,80,81], dioxins [82,83], arylamines [84,85], and heterocyclic amines [86,87].

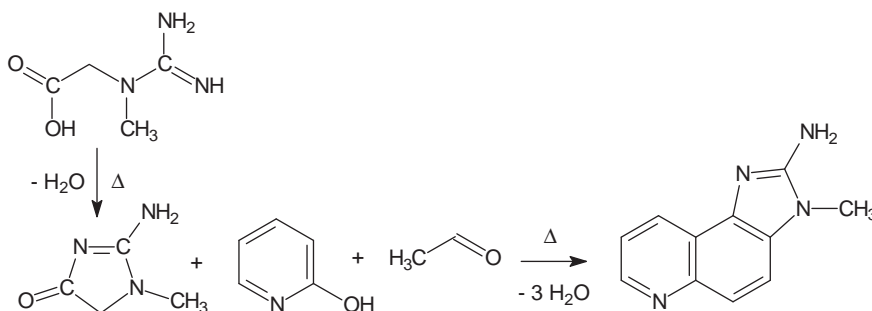
### **Pyrolysis products in food and cigarette smoke**

Food processing at elevated temperatures is of particular interest regarding pyrolytic reactions either regarding the generation of aromas [88,89] or the potential formation of toxic compounds, such as heterocyclic amines [90], which also have mutagenic and carcinogenic properties [91–93], or the

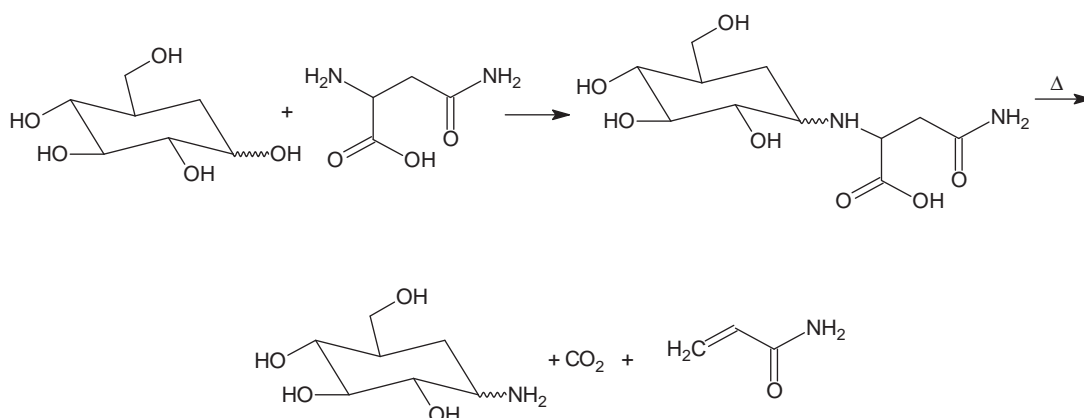
formation of other toxicants such as acrylamide [94]. Heterocyclic amines, for example, can be generated by the pyrolysis of amino acids such as glutamine [95], tryptophan [96], and others [49] and were detected in various types of cooked meat. For example, glutamine pyrolysis generates 2-aminodipyrido-[1,2-a:3',2'-d]imidazole (Glu-P-2) by eliminating water, as indicated in the following reaction:



More complicated reactions take place in food under the influence of heat involving compounds such as *N*-(aminoiminomethyl)-*N*-methylglycine (creatine), various pyridines, aldehydes, and amino acids. The formation of 2-amino-3-methylimidazo[4,5-f]quinoline (IQ) is shown in the following reaction:



Pyrolysis of polymeric and non-polymeric materials present in food, including those formed by Maillard reactions, also may generate various toxic compounds. The formation of acrylamide, for example, is attributed to the decomposition of a compound formed in a Maillard type reaction between a reducing sugar, such as glucose and asparagine, followed by pyrolysis:



Due to the composite nature of most food items, it is very difficult to identify a unique source for the pyrolysate components as originating from polymeric or non-polymeric materials. However, analytical pyrolysis is a useful technique for food characterization (e.g., [89]).

Cigarette smoke is an extremely complex pyrolysate, which is generated during the burning (smoldering) of a composite material consisting of plant parts and additives. Because of the widespread



habit of smoking and the related health concerns, numerous studies have been devoted to the pyrolysis processes taking place in a burning cigarette [49,97–105]. Similarly to the case of food pyrolysates, it is very difficult to identify a unique source for the cigarette smoke components as originating from polymeric or non-polymeric materials. However, a number of studies were dedicated to the pyrolysis of particular compounds present in cigarettes; these include various cigarette additives [5] and components of the cuticular wax of the tobacco leaf [106]. More frequently, the effort was focused toward the characterization of specific classes of compounds present in cigarette smoke such as PAHs [107–109], aromatic amines [110], pyridines [111], heterocyclic amines [112,113], carbonyl compounds [114–116], phenols [117,118], and dioxins [119].

The description of pyrolysate composition obtained from different classes of compounds, some present in food or in cigarettes, as well as the toxicological properties of the pyrolysates constituents, are discussed further in this book.

## 6.4. APPLICATIONS OF PYROLYSIS IN FORENSIC SCIENCE

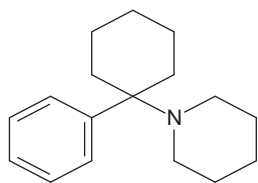
### *General aspects*

Analytical pyrolysis is a valuable forensic tool as proven by its common use in forensic laboratories and by the considerable number of publications related to this subject (see, e.g., [120–124]). The type of samples encountered in forensic investigations are diverse and may include traces of hair, fibers, paints, adhesives, plastics and rubbers, motor vehicle fluids, oils and fats, cosmetics, inks, and drugs. The ability of analytical pyrolysis to analyze polymeric and insoluble samples fits very well the analysis of these materials. In addition, forensic samples typically require sample identifications and comparisons with similar materials from a known source, rather than a quantitative measurement of a specific analyte. Also, the amount of sample from the offender side is typically extremely small. These requirements are well covered by the capabilities of analytical pyrolysis (such as Py-GC/MS) where only a very small amount of sample is necessary for complex comparisons. The results from analytical pyrolysis can be corroborated with information from other analytical techniques commonly used in forensic investigations such as microscopy (optical and scanning electron microscopy) and FTIR spectroscopy.

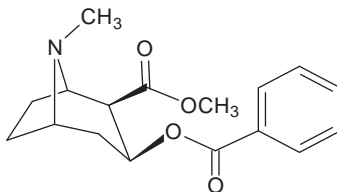
Very frequently, the materials requiring a forensic investigation are of polymeric nature, including synthetic polymers such as plastics, paints, and adhesives, or natural polymers such as natural fibers, hair, and natural varnishes. Examples of analyses of polymeric materials for forensic purposes can be found in various publications (see, e.g., [3,49,125,126]). Some other forensic applications involve pyrolysis of non-polymeric organic molecules and are related to the content of this book. A few examples from this category will be discussed further.

### *Applications to problems related to illicit drugs*

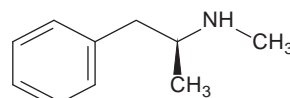
Use of a number of illicit drugs often involves smoking, which generates decomposition products and subsequently new biomarkers as a result of their metabolism. These include phencyclidine, cocaine, heroin, methamphetamine, and marijuana (with its main active component  $\Delta^9$ -tetrahydrocannabinol).



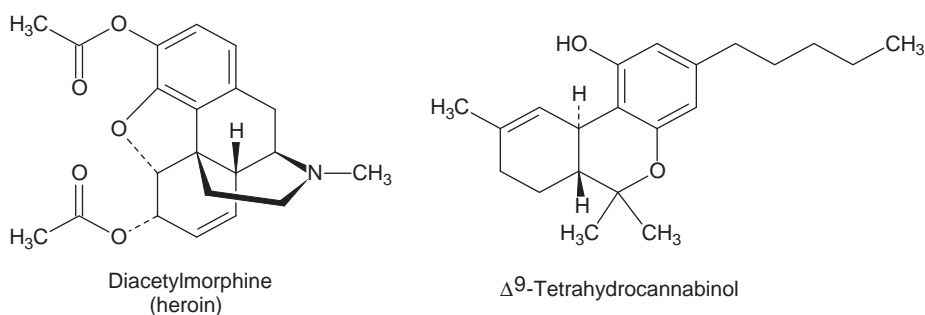
Phencyclidine



Cocaine



Methamphetamine



Some of these illicit drugs are smoked alone, and some can be mixed with tobacco and smoked [127]. Pyrolysis is used for various purposes in relation to these substances and their pyrolysis products [128]. For example, the different components found in the drug matrix may allow the characterization of a link between two illicit drugs [129, 130]. Traces of drugs can be analyzed using analytical pyrolysis. Also, pyrolytic products and metabolic degradation products show considerable similarities. For example, from cocaine, both cocaethylene and norcocaine are generated by pyrolysis and through metabolism [131]. Other degradation products are generated only by pyrolysis (such as anhydroecgonine methyl ester also known as methylecgonidine) or only by metabolism (such as benzoylecgonine). Pyrolytic studies on illicit drugs and on biological samples such as urine allow the detection of specific smoking biomarkers that may be of interest in the detection of a drug. Pyrolysis products can be used for simulating smoking conditions and provide information on which compounds should be analyzed for detecting a specific drug [124, 131].

### **Applications to the analysis of traces of lipids**

Lipids are common substances present in vegetable oils and animal fats. These include the lipids from the human skin surface, waxes and cosmetics, soaps, etc. The presence of these materials on a crime scene may be very important for solving a particular forensic question. A specific profile of the many organic acids that form the lipids can be used as a fingerprint for the fatty material. However, an analysis of fats performed on a very small amount of material can be a challenging task. Pyrolysis in the presence of an added reactant such as tetramethylammonium hydroxide (TMAH) or trimethyl-(trifluorotolyl)ammonium hydroxide (TMTFTH), which generates methyl esters of the fatty acids present in the lipid, has been used successfully for this type of analysis [132]. The use of TMTFTH has the advantage over TMAH of being less basic and inducing less isomerization for the acids with two or more sites of unsaturation. The reaction taking place during pyrolysis is a transesterification that changes the glycerol ester into a methyl ester. Using this procedure, a variety of fatty materials have been analyzed and differentiated. The samples include human skin lipids with a fatty acid profile that depends on individual and environmental factors, cosmetics such as body lotions and lipsticks that contain various lipids depending on the manufacturer, as well as lanolin, which is used in some cosmetics and has a fatty acid profile characteristic for the lanolin source.

### **Forensic analysis of fire debris**

An important amount of information for an investigation of a suspected arson can be obtained from the chemical analysis of the debris remaining after the fire. In these investigations, the main focus for the analysis is the detection and characterization of ignitable liquid residues. The National Center for Forensic Science holds a reference collection and a database of ignitable liquids [133]. The typical materials identified as present in arson cases include automobile gasoline and diesel fuels. The presence of these materials in the fire debris aids a fire investigator in determining whether or not arson should be suspected. However, it is a very difficult task to detect ignitable liquid residues in the background of the many chemicals generated during a fire from common building and household

materials such as plastic and wool carpets, wood, roofing materials, wallpaper, and from ignitable liquids that may be present by accident during the fire. Pyrolysis studies were performed on a variety of building and household materials with the purpose of establishing the types of background that may be expected during the analysis of fire debris [122,134]. This background can be obtained either using analytical pyrolysis instrumentation or by simulating in a laboratory setup the real process of partial burning typically encountered in a fire. The fire debris is typically extracted with an appropriate solvent (e.g., with CS<sub>2</sub>) and analyzed preferably with GC/MS instrumentation. The more volatile components of ignitable liquids may be absent from an extract of fire debris even if the liquid was present at the beginning of the fire. For this reason, a detailed study of various ignitable liquids in pyrolytic conditions is also useful.

### Other forensic applications

Many materials used as forensic evidence, including paints, adhesives, rubbers, plastics, motor vehicle body fillers, fibers, inks, etc., are of polymeric nature. However, they frequently contain non-polymeric molecules such as plasticizers, antioxidants, lubricants, antistatic agents, surfactants, fragrances, heat stabilizers, and fire retardants. These substances may have pyrolysis products that can be used, in addition to the polymer pyrolysates, for the identification/fingerprinting of a specific material. Examples of such applications can be found further in Part 2 of this book.

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## CHAPTER 7

*Pyrolysis of Hydrocarbons***7.1. ACYCLIC SATURATED HYDROCARBONS*****General aspects***

Acyclic saturated hydrocarbons (alkanes or paraffins) are hydrocarbons with the general formula  $C_nH_{2n+2}$  where  $n$  takes values from 1 to higher numbers. Only the compounds with  $n$  lower than about 50 can be considered small molecules and will be discussed further in this section. The compounds with  $n$  in the range between 50 and 500 are considered oligomers (hydrocarbon waxes). For values of  $n$  higher than about 500, the compounds are considered polymers. Typical values for  $n$  in polymers range between 500 and 1500 (MW = 15,000–40,000 for polyethylene), and the compounds are known as polyolefins. Detailed studies on the pyrolysis of polyolefins have been reviewed thoroughly in the literature (see, e.g., [1]). The pyrolysis of alkanes with  $n$  larger than about 20 shows strong qualitative similarities with the pyrolysis of the corresponding polymers. For example, the main pyrolysis products of both polyethylene and  $n$ -trtriacontane are linear alkenes (with various numbers of carbons), plus lower levels of alkanes and alkadienes. The level ratios in the pyrolysates of alkene/alkane or alkene/alkadiene (for fragment molecules with the same number of carbons) vary from compound to compound.

During pyrolysis some peculiarities are displayed by the molecules with low  $n$  (methane, ethane, etc.). Also, while the pyrolysis of higher molecular weight materials is typically studied using filament, Curie point, or micro-furnace pyrolyzers (common for analytical pyrolysis studies of solid samples), the pyrolysis of gaseous low-molecular-weight hydrocarbons is studied by different techniques. The equipment for these techniques includes static systems of relatively large volumes (about 500 mL) such as a quartz cylinder heated in a furnace [2], flow systems [3], or shock tubes [4]. The detection of species formed during pyrolysis is done either with the same techniques as for solid samples such as mass spectrometry or with more complex techniques (see Section 4.2).

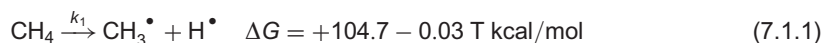
Pyrolysis of alkanes typically takes place by a radicalic mechanism, the radicals being formed by the cleavage of a C–C or a C–H bond. However, a simple C–C bond has a dissociation energy of 83–85 kcal/mol while a C–H bond has a dissociation energy of 96–99 kcal/mol (see Table 3.1.1). This indicates that the probability of cleavage for a C–C bond is higher, and these bonds will start cleaving at lower temperatures than the C–H bonds. From Table 3.1.2, some differences are seen between the dissociation energies of C–C bonds where the carbons are primary, secondary, etc. As an example, the dissociation energy for the C–C bond in ethane is 88.2 kcal/mol, while the dissociation of the C–C bond in a compound of the type  $R_2HC-CR_2H$  requires 76 kcal/mol. As a general rule, the more substituted are the carbon atoms participating in a bond, the lower is the dissociation energy of the bond. The decrease in the bond energy with the increase in substitution of the carbon atom is also applicable to the C–H bonds. These rules may show variations depending on the true nature of the substituents. Larger differences in the bond dissociation energy influence the pyrolysis outcome but small differences do not.

***Methane***

Methane ( $CH_4$ ) is found in nature in large accumulations either alone (with purities between 93% to 99%) or in the gases associated with oil deposits. Methane can be found also in coal mines. Besides being used as a combustible, methane is used widely in industrial processes as a source of hydrogen (obtained from methane by an oxidative pyrolysis process). Its non-oxidative pyrolysis is used in industry mainly for the production of acetylene and of carbon black. Because of its numerous practical applications, pyrolysis of methane is the subject of a very large number of studies and publications (see, e.g., [5–8]).

Pyrolysis of methane is a complex process, which takes place through many free radical reactions. These include initiation, propagation, and termination reactions (see Section 2.2). An extensive list of these reactions and their associated rate constants during methane pyrolysis or pyrolysis/oxidation has been reported [9]. The temperature and pressure of the gas are important factors influencing the path of the pyrolytic reactions. Catalysis on the walls of reaction vessels also may influence the results.

In gas phase at about 1000 K, the first reaction during methane pyrolysis (initiation step) is the dissociation with the formation of the methyl radical ( $\text{CH}_3^\bullet$ ) and atomic hydrogen, as shown below (see Table 3.1.2 for the bond dissociation energy):



Another potential reaction of methane upon heating was considered to be the formation of methylene  $\text{CH}_2^{\bullet\bullet}$  biradical and a hydrogen molecule  $\text{H}_2$  by the following reaction:



However, the methylene formation (considering the enthalpy component only) is slightly more endothermic than that of methyl ( $\Delta H = +109 \text{ kcal/mol}$  compared to  $104 \text{ kcal/mol}$ ), and kinetics studies showed that the frequency factor for the reaction 7.1.2 is considerably lower than that for reaction 7.1.1. Overall, it was estimated that the reaction with the formation of methylene and hydrogen molecule is about 1000 times slower than the reaction with methyl radical formation [2]. Also, studies of pyrolysis of a mixture of  $\text{CH}_4$  and  $\text{CD}_4$  showed that HD does form during pyrolysis (D is  $^2\text{H}$ ). Reaction 7.1.1 on a mixture of  $\text{CH}_4$  and  $\text{CD}_4$  predicts the formation of HD as a result of the combination of hydrogen and deuterium atoms. On the other hand, reaction 7.1.2 does not predict the formation of HD because only  $\text{H}_2$  and  $\text{D}_2$  are formed by that mechanism. It can be concluded that reaction 7.1.1 dominates the beginning of methane pyrolysis.

The entropic factor may play some role in the overall result of chemical reactions 7.1.1 and 7.1.2. As shown in Section 3.1, chemical equilibria are determined by the free enthalpy, which, in addition to the enthalpy value  $\Delta H$ , includes the term  $T\Delta S$ , which is directly dependent on temperature. One problem in considering the free enthalpy instead of enthalpy of these reactions is the scarce information regarding the entropy values for the reaction participants. On the other hand, when the number of molecular species in the reactions is the same, the variations in entropy values should not be very different. For this reason, for reactions 7.1.1 and 7.1.2 (as well as for most of the reactions discussed further in this chapter), comparisons will be made based on enthalpy values instead of being made on free enthalpy values. The dependence on temperature of the enthalpy frequently is neglected in these comparisons (see Section 3.1).

Typical for unimolecular reactions (see Section 3.2), the rate constant for reaction 7.1.1 is dependent on the methane pressure (in a certain range). The values for the rate constant at different temperatures and pressures are reported in the literature [2,10]. Figure 7.1.1a–d show the variation of  $k_1$  as a function of pressure at different temperatures [2].

For each temperature, a low-pressure rate constant  $k^0$  (where the reaction becomes of second order) and a limiting high-pressure rate constant  $k^\infty$  (where the reaction is truly of first order and does not depend anymore on pressure) were determined [2]. From these data, the frequency factor in Arrhenius reaction rate equation (see rel. 3.2.5) was determined  $A^\infty = 2.8 \times 10^{16} \text{ s}^{-1}$ , and the activation energy  $E^\infty = 107.6 \text{ kcal/mol}$  [2].

The formation of methyl and hydrogen radicals at about 1000 K is followed by the sequence of reactions shown below:



The overall result is the formation of  $\text{C}_2\text{H}_6$  and of molecular hydrogen:





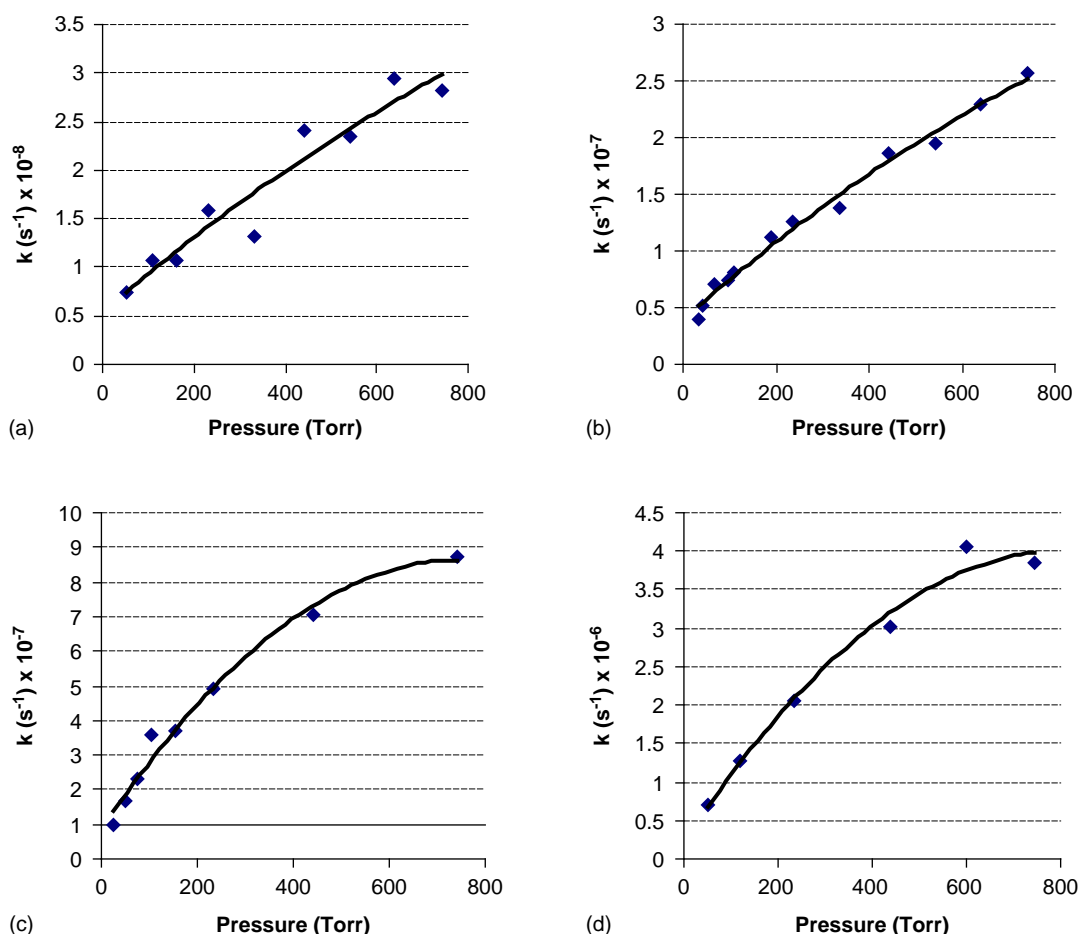
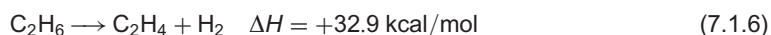


FIGURE 7.1.1. a. Variation of  $k_1$  with  $\text{CH}_4$  pressure at  $995\text{ K}$  [2]. b. Variation of  $k_1$  with  $\text{CH}_4$  pressure at  $1038\text{ K}$  [2]. c. Variation of  $k_1$  with  $\text{CH}_4$  pressure at  $1068\text{ K}$  [2]. d. Variation of  $k_1$  with  $\text{CH}_4$  pressure at  $1103\text{ K}$  [2].

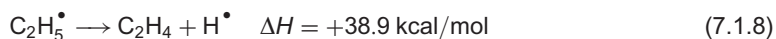
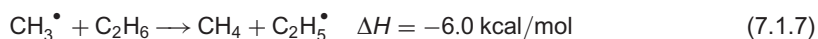
The previous reactions represent a Stage 1 in methane pyrolysis. Additional detailed information regarding the kinetics of the reactions in this stage can be found in the literature [2,11–13].

The formation of hydrogen molecules and of ethane, without the formation of noticeable amounts of other pyrolysis products, lasts a very short period of time, and traces of other compounds (such as ethylene and acetylene) are formed in a few seconds. Figure 7.1.2 gives the variation in time of the composition of gases when  $\text{CH}_4$  is heated at  $1038\text{ K}$  and at  $441\text{ Torr}$  [2]. The changes in the concentration of different reaction products are strongly affected by temperature and gas pressure.

While the reactions from Stage 1 continue, under the influence of heat the formed  $\text{C}_2\text{H}_6$  starts a dehydrogenation reaction to generate ethene (ethylene) as follows:



The steps in this process are the following:



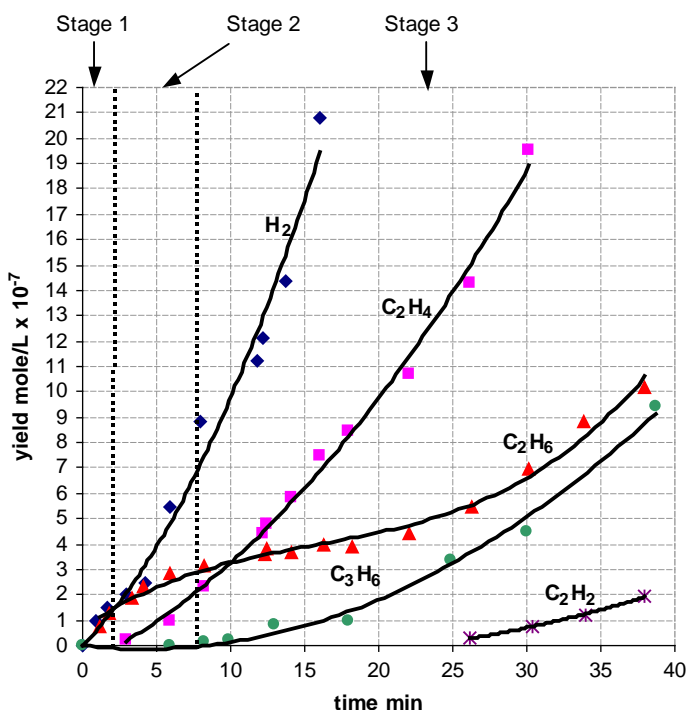


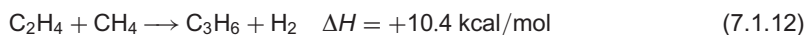
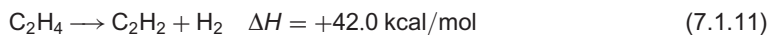
FIGURE 7.1.2. Yields of pyrolysis products from methane in a static system at 1038 K at 441 Torr as a function of time [2].

As larger concentrations of C<sub>2</sub>H<sub>6</sub> appear, ethane also undergoes a unimolecular decomposition that takes place with the formation of methyl radicals (see Table 3.1.2 for the bond dissociation energy):

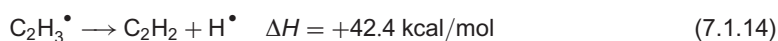
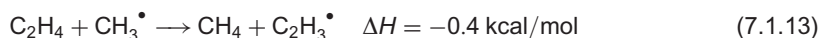


Since reaction 7.1.10 is strongly endothermic, it is favored by higher temperatures. Reactions 7.1.6 and 7.1.10 can be considered to form a Stage 2 of pyrolysis, where the rate of formation of C<sub>2</sub>H<sub>6</sub> slows down and the formation of C<sub>2</sub>H<sub>4</sub> starts, as shown in Figure 7.1.2. For the set of reactions 7.1.6–7.1.10, the reaction rate constants at different temperatures and at different values of the CH<sub>4</sub> pressure were reported in the literature [14].

The continuation of heating of the gas mixture results in further complication of the pyrolytic processes. In what can be considered a Stage 3 of the process, ethylene formed in the previous stage undergoes subsequent reactions, forming acetylene and propene (propylene) as shown below:

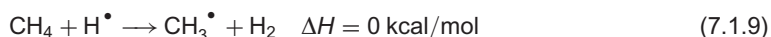
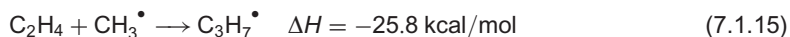


The acetylene formation is the result of the following reactions:

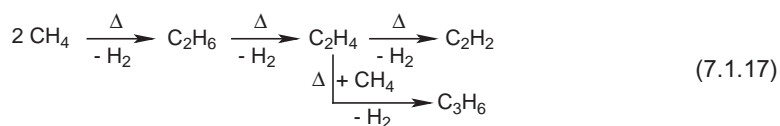


As seen from reactions 7.1.13, 7.1.14, and 7.1.9, the formation of acetylene does not occur from the direct dehydrogenation of  $C_2H_4$  but (mainly) as a result of the interaction of ethylene with the free radicals previously formed in methane decomposition.

The chain of reactions leading to the formation of propene can be written as follows:



Several thermodynamic and kinetic parameters of the reactions in Stage 3 of methane pyrolysis are reported in the literature [15]. The chain of reactions that explain the gas composition shown in Figure 7.1.2 can be summarized by the following sequence:



Further pyrolysis of methane, as a result of the reactions of the products generated in the first three stages of pyrolysis, becomes very complex. In reactions with mechanisms similar to those previously described, alkenes, cycloalkenes (such as cyclopentadiene), and alkynes are formed, containing three, four, and more carbon atoms. The continuation of heating leads to the generation of aromatic hydrocarbons such as benzene, toluene, styrene, naphthalene, anthracene, and fluoranthene, ending with soot [15]. Soot is composed mainly of carbon, although its structure is more complicated being formed from many condensed aromatic rings (typical basic structures being units of 61 or 91 rings and formulas  $C_{150}H_{30}$  and  $C_{216}H_{36}$ , respectively). An idealized soot structure is shown in Figure 7.1.3. Even larger basic structures are known, having a lower number of hydrogen atoms per unit. The true soot structure is less regular, and five-ring cycles and aromatic rings in a sequential form rather than condensed order also may be present. The basic units are aggregated to form particles of 0.01–5  $\mu\text{m}$  diameter.

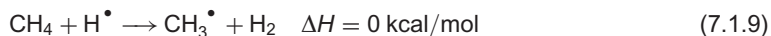
Computer simulation of methane pyrolysis [7] allowed taking into consideration a large number of potential reactions. Among these reactions involved in the initiation, propagation, and termination of methane pyrolysis are dissociations, recombinations, radical additions to double or triple bonds between two molecules or intramolecular,  $\beta$ -scissions, H-abstractions, radical disproportionations, H transfers to an unsaturated carbon with radical formation, intraradical H migration, etc. The initial carbon deposited in these reactions may have some catalytic role in further carbon deposition [16].

A higher temperature for the pyrolysis accelerates the decomposition and increases the yield of carbon. The variation in time of the yield of benzene, toluene, and carbon (and of  $C_2H_4$ ) at 1118 K at 307 Torr of methane is shown in Figure 7.1.4 [15].

At higher temperatures, additional reaction types to those shown for the sequence of reactions 7.1.17 may take place during methane pyrolysis. For example, the study of pyrolysis around 2600 K [17] indicates that direct formation of  $C_2H_4$  is possible by the reaction:



Reaction 7.1.18 is the result of the following sequence:



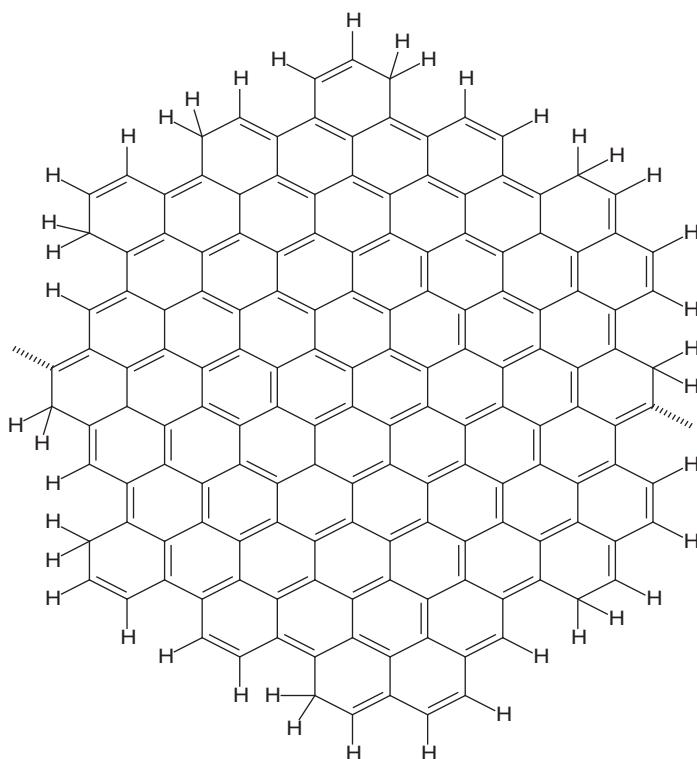
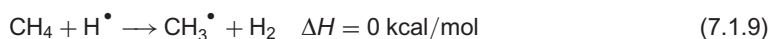
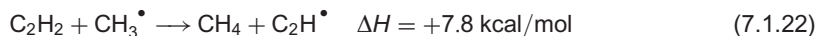


FIGURE 7.1.3. Idealized structure of a basic unit of soot.

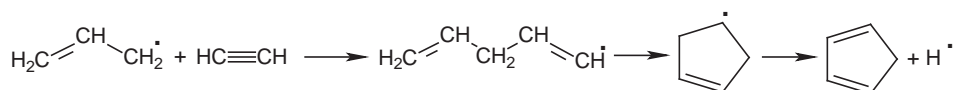
Other reactions are also possible at higher temperatures. For example, acetylene may undergo a decomposition reaction as follows:



The steps in this process are shown below:



As seen from reactions 7.1.21, 7.1.23, and 7.1.9, the formation of carbon does not occur from the direct dehydrogenation of  $\text{C}_2\text{H}_2$  but as a result of the interaction of acetylene with the free radicals previously formed in methane decomposition. Even so, since reaction 7.1.21 is very endothermic, it does not take place at temperatures below 1200 K, when the carbon seems to be formed from high-molecular-weight compounds following polymerization and hydrogen elimination. Two compounds with a role in these reactions seem to be butadiene and cyclopentadiene, which are generated in the pyrolytic process of methane after acetylene starts forming. The reactions leading to cyclopentadiene are the following:



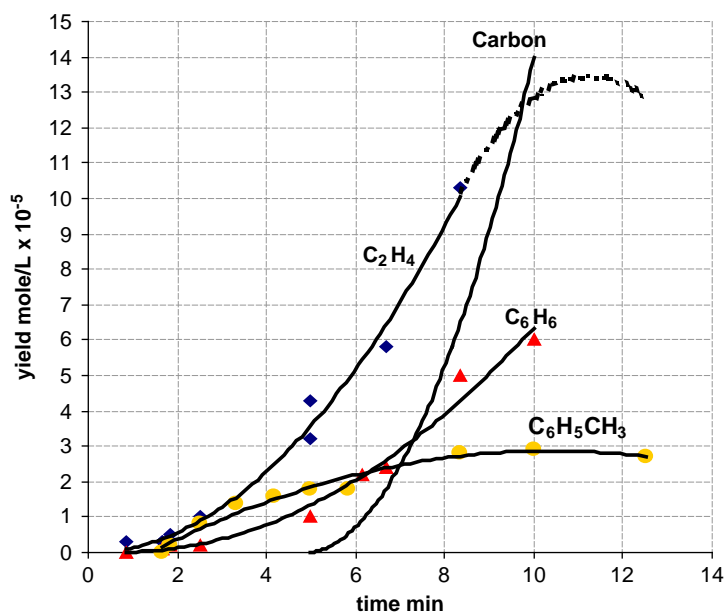
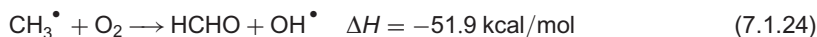


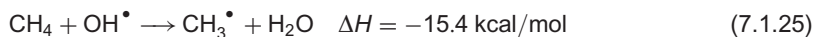
FIGURE 7.1.4. Yields of pyrolysis products from methane in a static system at 1118 K at 307 Torr as a function of time [15].

Cyclopentadiene can cause chain branching by radicalic mechanisms [18]. Butadiene, cyclopentadiene, and similar compounds may undergo Diels–Alder type condensation reactions leading to the formation of compounds with higher molecular weight [6,19]. The same higher molecular weight compounds also can be formed by reactions with radicalic mechanisms (see reactions 2.5.2–2.5.4) considering that Diels–Alder condensations are not favored by the increase in the temperature.

Pyrolysis of methane in the presence of other gases also was thoroughly studied. Of particular interest was the pyrolysis in the presence of oxygen usually diluted with an inert gas, for example, argon [4,20]. Nitrogen or steam can be used for practical purposes as a diluent. Pyrolytic oxidation of methane is related to important practical applications such as generation of CO and hydrogen mixture used in various organic syntheses, for example, of  $\text{CH}_3\text{OH}$ . A considerably large number of reactions occur when methane, oxygen, and an inert gas are heated together [4]. The predominance of specific reactions is a function of temperature and the composition of the gas mixture. Oxidative pyrolysis includes a pyrolysis step that was found to be an important part of the oxidation mechanism. For example, after reaction 7.1.1 occurs, among other reactions in the presence of oxygen, the methyl radicals react as follows:



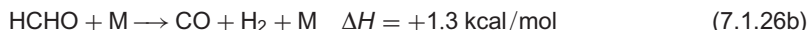
The rate coefficients in Arrhenius equation for this reaction are  $A = 2.3 \times 10^{12}$  and  $E^\ddagger = 20.3 \text{ kcal/mol}$ . The  $\text{OH}^\bullet$  radicals can react further with  $\text{CH}_4$  as shown below:



As a function of temperature, pressure, and gas mixture composition, oxidative pyrolysis of methane also generates CO. This substance can be formed, for example, starting with the further decomposition of formaldehyde in the presence of heat as follows:



The reaction should be written including the interaction of the inert component M:



The presence of an excess of  $\text{O}_2$  leads to further reactions with  $\text{H}_2$  and  $\text{CO}$ , the end result being the formation of  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CO}_2$ , the ratio  $\text{CO}/\text{CO}_2$  depending on the initial  $\text{CH}_4/\text{O}_2$  ratio.

The formation of peroxides in the reaction between the free radicals generated in the first pyrolysis stage and the oxygen was also found to be part of methane oxidation in the burning process. This type of reaction occurs as follows:



In addition to the end reaction 7.1.27c, formation of more free radicals may occur since the peroxide  $\text{CH}_3\text{OOH}$  is unstable at elevated temperatures and can decompose with the formation of two free radicals as shown below:



These additional free radicals may accelerate further the oxidation process. The radical  $\text{CH}_3\text{O}^\bullet$  by hydrogen abstraction generates  $\text{CH}_3\text{OH}$  detected during the incomplete combustion of methane [21]. Formation of hydroperoxide radicals  $\text{OOH}$  was suggested to be a component reaction during the oxidation process [7]. The complete combustion of methane to form  $\text{H}_2\text{O}$  and  $\text{CO}_2$  generates 191.7 kcal/mol, making methane an important source of energy. The formation of polycyclic aromatic hydrocarbons (PAHs) in methane flames [22,23] is a subject of considerable importance due to the carcinogenic characteristics of this class of compounds (see Section 7.8).

The complexity of reactions occurring during pyrolysis/oxidation of methane has been studied using computer modeling, which allows the calculation of the composition of the resulting gas mixture at specific initial component ratios, temperatures, pressures, and time along the reaction path [4]. A number of computer programs are described in the literature [24] for modeling the experimental information using available kinetic data regarding methane pyrolysis.

Catalytic pyrolysis and catalytic oxidative pyrolysis of methane are subjects extensively studied and published [16,25–28]. The pyrolytic and oxidative pyrolytic processes of methane have been studied on various catalysts including silica, activated carbon, and metals, with purposes such as the reduction of  $\text{CO}_2$  emissions during  $\text{H}_2$  production from methane [29] and better yields of specific compounds in the pyrolysate [26].

## Ethane

Ethane ( $\text{C}_2\text{H}_6$ ) is present in nature in petroleum gas and as a minor component in natural gas (between 1% and 7%). Pyrolysis of ethane is used extensively for the production of ethylene ( $\text{C}_2\text{H}_4$ ). This pyrolysis is performed for industrial purposes in the presence of steam around 900 °C (steam cracking). The steam is used as a diluent for ethane pyrolysis. Mainly due to the high practical importance of ethylene produced from ethane, the pyrolysis of ethane is the subject of a very large number of studies (see, e.g., [30–32]) and patents. Preparation of ethylene from ethane is a particularly important industrial process since ethylene is the raw material for the production of polyethylene.

The decomposition of ethane under the influence of heat takes place by a free radical mechanism, similar to that indicated for methane. Two possible unimolecular reactions were considered as the initiation step (see Table 3.1.2 for the bond dissociation energy):



and



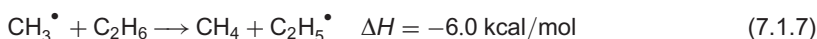
Since reaction 7.1.29 is more endothermic, reaction 7.1.10 is dominant in ethane decomposition. As a typical unimolecular reaction (see Section 3.2) an interval of pressure for which the reaction rate is dependent on  $\text{C}_2\text{H}_6$  pressure was noticed, and a low-pressure rate constant  $k^0$  and a limiting high-pressure rate constant  $k^\infty$  were determined for this reaction [33–35]. For the limiting high pressure, the frequency factor in Arrhenius reaction rate equation was determined  $A^\infty = 5.2 \times 10^{16} \text{ s}^{-1}$ , and the activation energy  $E^\infty = 88.8 \text{ kcal/mol}$  [35]. The work for determining these constants was carried out at temperatures around  $900^\circ\text{C}$ .

The generation of free radicals following ethane scission has as a main result the following process (see methane):



Reaction 7.1.6 was written previously as part of methane decomposition, resulting from the sequence of reactions 7.1.7–7.1.9 that lead to  $\text{C}_2\text{H}_4$  formation. At about  $1073 \text{ K}$  reaction 7.1.6 attains equilibrium ( $K_p \approx 1$ ). For industrial purposes this reaction is commonly performed in 50 mol % steam, and the weight conversion of ethane can reach 78.1% [30].

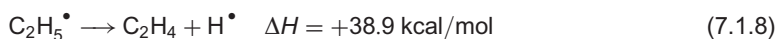
The methyl radicals formed in reaction 7.1.10 further react with ethane as previously shown for methane:



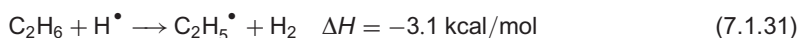
The kinetics of this reaction shows deviation from Arrhenius behavior, and its rate constant depends on the temperature by an empirical equation of the form [36]:

$$k = 1.82 \times 10^3 T^4 \exp \left[ \frac{-8.2 \text{ kcal/mol}}{RT} \right] \text{ L/mol/s} \quad (7.1.30)$$

Ethyl radical decomposition generates ethylene, as already shown in the discussion for methane pyrolysis:



The active hydrogen atoms  $\text{H}^\bullet$  will react further with the ethane excess generating more ethyl radicals as follows:



The parameters in Arrhenius equation for reaction 7.1.31 in the range  $350\text{--}1250 \text{ K}$  were determined to be  $A = 1.3 \times 10^{11} \text{ s}^{-1}$ , and the activation energy  $E^\ddagger = 9.4 \text{ kcal/mol}$  [37]. Hydrogen atoms participate in other abstraction reactions including those with traces of methane (formed, e.g., in reaction 7.1.7), as shown by reaction 7.1.9.

Besides the propagation reactions, the recombination reactions between  $\text{H}^\bullet$ ,  $\text{CH}_3^\bullet$ , and  $\text{C}_2\text{H}_5^\bullet$  radicals contribute to the formation of final reaction products, including larger molecules such as butane. The variation in the mole fraction of ethane, ethylene, and methane in a pyrolysis experiment performed in a flow system with the average temperature of  $1185 \text{ K}$  (reactor entrance  $900 \text{ K}$  and  $1200 \text{ K}$  in the middle of the reactor),  $300 \text{ Torr}$ , and a flow rate of  $484 \mu\text{g/s}$  is shown in Figure 7.1.5 [38].

Numerous other reactions take place during ethane pyrolysis [9,39–42]. A detailed study of the induction period in ethane pyrolysis and the precise evaluation of some thermodynamic parameters of ethyl radical are described in the literature [42]. Depending on pyrolysis temperature, further decomposition of ethylene formed from ethane leads to the formation of acetylene (as shown by

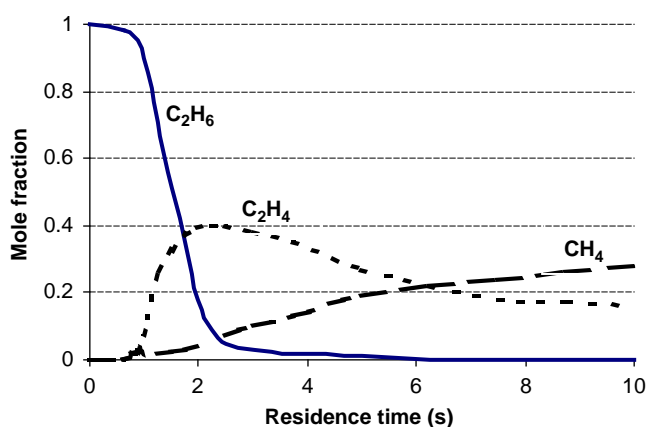


FIGURE 7.1.5. Variation in the molar ratios of ethane, ethylene, and methane in a flow system with the average temperature of 1185 K [38].

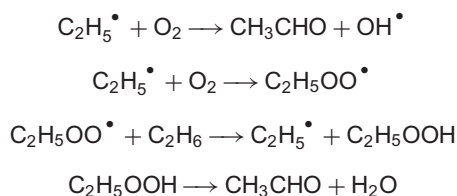
reaction 7.1.11) and, at high temperatures, to the deposition of carbon as shown in the sequence of reactions below:



Side reactions with the formation of  $\text{C}_3\text{H}_6$  (as shown for methane) and the formation of other hydrocarbons are known to occur. Besides hydrogen, methane, ethylene, acetylene, and carbon, which are the main pyrolysis products at temperatures up to 1200 °C, other compounds were identified at lower levels in ethane pyrolysates. Among these are propene, propyne, butane, butene, cyclopentadiene, 1,3-butadiene, fulvene, 1,2-butadiene, vinylacetylene, and benzene [39].

The formation of acetylene in the chain of reactions 7.1.32 is not a simple dehydrogenation reaction, which would be thermodynamically unfavorable, but the result of various interactions of free radicals and molecules formed during pyrolysis. Similarly the carbon formation is very likely the end result of formation of heavier molecules generated as a result of condensations and other reactions.

Similar to the case of methane, the pyrolytic oxidation of ethane was studied extensively [43–45]. An inert gas for dilution frequently was used in these studies. Depending on the proportion ethane/oxygen/inert gas, the result of ethane oxidation differs. Complete combustion of ethane leads to the formation of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , with the generation of 373 kcal/mol. The process takes place by a complex series of free radical reactions in which pyrolysis is an essential part. A large number of reactions that may take place during ethane oxidation were considered in computer modeling (simulation) programs [24,43]. In one such program, ethane oxidation was simulated using 157 elementary reactions with known or estimated rate constant parameters  $A$ ,  $n$ ,  $E^\ddagger$  (or  $E^a$ ),  $k^0$ ,  $k^\infty$ , and Troe parameters [43]. The programs allow the calculation of resulting gas composition at a specified time, in given conditions of temperature, pressure, and initial gas composition. Upon the agreement of the predicted and calculated values for the pyrolysate (or flame) composition, it is possible to determine the main reaction paths followed during pyrolysis and to adjust some of the kinetic parameters of these reactions (similar to the modeling of oxidative pyrolysis of methane). Among the reactions that have an important role during the oxidation of ethane are reactions similar to those in methane oxidation where the  $\text{CH}_3$  group is replaced by  $\text{C}_2\text{H}_5$  group as follows:



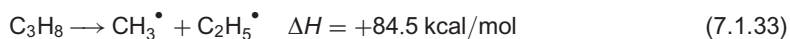


Besides pyrolysis of pure ethane, its pyrolysis in the presence of other compounds such as heavier hydrocarbons was studied. The heavier hydrocarbons seem to accelerate ethane decomposition with ethylene formation at moderate conversions, and the opposite effect is noticed at higher conversions [46]. The production of ethylene is increased at moderate conversions and decreased at higher conversions by the presence of heavier hydrocarbons. Alkenes addition seems to decrease the reaction rate of ethane decomposition. Pyrolysis in the presence of steam and catalytic pyrolysis were studied, mainly related to carbon deposition (coke formation), which is undesirable in ethylene production (see, e.g., [47]). The steam (H<sub>2</sub>O) seems to affect the interactions with the surfaces during pyrolysis and decreases the carbon deposition. In homogeneous pyrolysis, steam acts only as a diluent. Addition of compounds such as H<sub>2</sub>PtCl<sub>6</sub> in the presence of steam can reduce significantly the carbon deposition [41].

### Propane

Propane (C<sub>3</sub>H<sub>8</sub>) is present in nature in petroleum gas and as a minor component in natural gas, the same as ethane but typically in lower proportions. Propane pyrolysis plays an important industrial role, mainly in the synthesis of propene, which is used, for example, for producing polypropylene.

The initial step in pyrolysis of propane is dominated by the initiation reaction:



The Arrhenius equation for the (forward) reaction 7.1.33 was found to be the following [48]:

$$k = 2 \times 10^{16} \exp \left[ \frac{-84.5 \text{ kcal/mol}}{RT} \right] \text{ s}^{-1} \quad (7.1.34)$$

Because side reactions of the initiation reaction 7.1.33 occur very fast, the reaction rate given by expression 7.1.34 is only an extrapolation of the results obtained for more advanced stages of the reaction [49]. The result of the formation of ethyl and methyl free radicals is a chain of other reactions (propagation and termination reactions). Two major products are formed in the pyrolysis, as shown below:



At 1073K in 50 mol % steam, 90% of propane is converted mainly into ethylene, propylene, methane, and hydrogen. However, besides the radicals indicated in reaction 7.1.33, a large number of other radicals were detected in propane pyrolysis. A list of these radicals containing up to seven carbon atoms is given in Table 7.1.1 [50]. The results were generated in experiments of depositing a matrix of polycarbon on carbon fibers by pyrolysis, a process called *chemical vapor infiltration* or CVI.

TABLE 7.1.1. Radicals up to seven carbon atoms detected during propane pyrolysis between 1173K and 1298K in a CVI experiment [50]

Name	Formula	Structure
Atomic hydrogen	H	H <sup>•</sup>
Methyne (carbyne)	CH	CH <sup>•••</sup>
Methylene (carbene)	CH <sub>2</sub>	CH <sub>2</sub> <sup>••</sup>
Methyl	CH <sub>3</sub>	CH <sub>3</sub> <sup>•</sup>
Ethynyl	C <sub>2</sub> H	CH≡C <sup>•</sup>
Ethenyl	C <sub>2</sub> H <sub>3</sub>	CH <sub>2</sub> =CH <sup>•</sup>
Ethyl	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub> <sup>•</sup>
	C <sub>3</sub> H <sub>2</sub>	C <sup>••</sup> =C=CH <sub>2</sub>

(Continued)

TABLE 7.1.1. *cont'd*








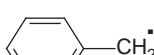
Name	Formula	Structure
Propynyl	C <sub>3</sub> H <sub>3</sub>	CH≡C-CH <sub>2</sub> •
	C <sub>3</sub> H <sub>5</sub>	CH•=CH-CH <sub>3</sub>
Propenyl	C <sub>3</sub> H <sub>5</sub>	CH <sub>2</sub> =CH-CH <sub>2</sub> •
2-Propenyl	C <sub>3</sub> H <sub>5</sub>	CH <sub>3</sub> -C•=CH <sub>2</sub>
Propyl	C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> •
2-Propyl	C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub> -CH•-CH <sub>3</sub>
	C <sub>4</sub> H <sub>3</sub>	CH•=CH-C≡CH
	C <sub>4</sub> H <sub>5</sub>	CH <sub>2</sub> =CH-C•=CH <sub>2</sub>
	C <sub>4</sub> H <sub>5</sub>	CH <sub>2</sub> =CH-CH=CH•
	C <sub>4</sub> H <sub>5</sub>	CH <sub>2</sub> •-CH <sub>2</sub> -C≡CH
	C <sub>4</sub> H <sub>5</sub>	CH <sub>3</sub> -CH•-C≡CH
	C <sub>4</sub> H <sub>5</sub>	CH <sub>3</sub> -C≡C-CH <sub>2</sub> •
Buten-4-yl	C <sub>4</sub> H <sub>7</sub>	CH <sub>2</sub> =CH-CH <sub>2</sub> -CH <sub>2</sub> •
Buten-3-yl	C <sub>4</sub> H <sub>7</sub>	CH <sub>2</sub> =CH-CH•-CH <sub>3</sub>
Butyl	C <sub>4</sub> H <sub>9</sub>	CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> •
2-Butyl	C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub> -CH <sub>2</sub> -CH•-CH <sub>3</sub>
2-Methyl-2-propyl	C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub> -C•(CH <sub>3</sub> )-CH <sub>3</sub>
Cyclopentadienyl	C <sub>5</sub> H <sub>5</sub>	
	C <sub>5</sub> H <sub>5</sub>	CH≡C-CH <sub>2</sub> -CH=CH•
Cyclopentenyl	C <sub>5</sub> H <sub>7</sub>	
	C <sub>5</sub> H <sub>7</sub>	CH <sub>2</sub> =CH-CH•-CH=CH <sub>2</sub>
	C <sub>5</sub> H <sub>7</sub>	CH <sub>2</sub> =CH-CH <sub>2</sub> -CH=CH•
Penten-3-yl	C <sub>5</sub> H <sub>9</sub>	CH <sub>2</sub> =CH-CH•-CH <sub>2</sub> -CH <sub>3</sub>
	C <sub>6</sub> H <sub>4</sub>	
	C <sub>6</sub> H <sub>5</sub>	CH•=CH-CH=CH-C≡CH
Phenyl	C <sub>6</sub> H <sub>5</sub>	
1-Methylcyclopentadien-1-yl	C <sub>6</sub> H <sub>7</sub>	
	C <sub>6</sub> H <sub>7</sub>	CH <sub>2</sub> =CH-CH=CH-CH=CH•
	C <sub>6</sub> H <sub>7</sub>	
	C <sub>6</sub> H <sub>9</sub>	CH <sub>2</sub> =CH-CH=CH-CH <sub>2</sub> -CH <sub>2</sub> •
	C <sub>6</sub> H <sub>9</sub>	
Benzyl	C <sub>7</sub> H <sub>7</sub>	

TABLE 7.1.2. Compounds with up to seven carbon atoms in the molecule detected during propane pyrolysis between 1173 K and 1298 K in a CVI experiment [51]

Name	Formula	Name	Formula
Hydrogen	H <sub>2</sub>	2-Methylbut-1-en-3-yne	C <sub>5</sub> H <sub>6</sub>
Methane	CH <sub>4</sub>	Cyclopentadiene	C <sub>5</sub> H <sub>6</sub>
Acetylene	C <sub>2</sub> H <sub>2</sub>	Penta-1,3-diene	C <sub>5</sub> H <sub>8</sub>
Ethylene	C <sub>2</sub> H <sub>4</sub>	2-Methylbuta-1,3-diene	C <sub>5</sub> H <sub>8</sub>
Ethane	C <sub>2</sub> H <sub>6</sub>	Cyclopentene	C <sub>5</sub> H <sub>8</sub>
Allene	C <sub>3</sub> H <sub>4</sub>	2-Pentene ( <i>cis</i> and <i>trans</i> )	C <sub>5</sub> H <sub>10</sub>
Prop-1-yne	C <sub>3</sub> H <sub>4</sub>	Pentane	C <sub>5</sub> H <sub>12</sub>
Prop-1-ene	C <sub>3</sub> H <sub>6</sub>	Hexa-1,3,5-triyne	C <sub>6</sub> H <sub>2</sub>
Propane	C <sub>3</sub> H <sub>8</sub>	Hex-3-ena-1,5-diyne	C <sub>6</sub> H <sub>4</sub>
Buta-1,3-diyne	C <sub>4</sub> H <sub>2</sub>	Hexa-1,3-dien-5-yne	C <sub>6</sub> H <sub>6</sub>
Vinylacetylene	C <sub>4</sub> H <sub>4</sub>	Benzene	C <sub>6</sub> H <sub>6</sub>
Buta-1,2,3-triene	C <sub>4</sub> H <sub>4</sub>	Hexa-1,3,5-triene	C <sub>6</sub> H <sub>8</sub>
Cyclobutene	C <sub>4</sub> H <sub>6</sub>	Cyclohexa-1,3-diene	C <sub>6</sub> H <sub>8</sub>
1,3-Butadiene	C <sub>4</sub> H <sub>6</sub>	5-Methylcyclopenta-1,3-diene	C <sub>6</sub> H <sub>8</sub>
1,2-Butadiene	C <sub>4</sub> H <sub>6</sub>	1,5-Hexadiene	C <sub>6</sub> H <sub>10</sub>
1-Butyne	C <sub>4</sub> H <sub>6</sub>	Cyclohexene	C <sub>6</sub> H <sub>10</sub>
2-Butyne	C <sub>4</sub> H <sub>6</sub>	3-Hexene ( <i>cis</i> and <i>trans</i> )	C <sub>6</sub> H <sub>12</sub>
1-Butene	C <sub>4</sub> H <sub>8</sub>	Hexane	C <sub>6</sub> H <sub>14</sub>
2-Butene	C <sub>4</sub> H <sub>8</sub>	Toluene	C <sub>7</sub> H <sub>8</sub>
2-Methyl-1-propene	C <sub>4</sub> H <sub>8</sub>	5,5-Dimethylcyclopenta-1,3-diene	C <sub>7</sub> H <sub>10</sub>
Butane	C <sub>4</sub> H <sub>10</sub>	3-Methylhexa-1,5-diene	C <sub>7</sub> H <sub>12</sub>
2-Methylpropane	C <sub>4</sub> H <sub>10</sub>		

The CVI process was performed at temperatures between 1173 K and 1298 K, the propane at partial pressures of 2.6 Torr diluted in nitrogen (total pressure 20.3 Torr) [51,52].

The presence of this large variety of free radicals leads to the formation of many different pyrolysis products consisting mainly of hydrogen, methane, ethylene, and acetylene. Other compounds including those previously indicated and not having more than seven carbon atoms in the molecule are shown in Table 7.1.2. The computer modeling of the pyrolysis of propane involved 386 possible chemical reactions, which allowed the prediction of the reaction outcome, the identification of major reaction paths in the process, and the evaluation of some of the kinetic parameters of the pyrolysis.

Further search for heavier compounds formed during propane pyrolysis [53] showed the presence of compounds as heavy as ethynylpyrene. Radicals heavier than seven carbon atoms are involved in the generation of these compounds [53]. The list of the compounds with more than seven carbon atoms in the molecule identified in propane pyrolysis in the conditions previously described (in a CVI experiment) is given in Table 7.1.3. The molar fraction of all compounds depends on temperature, but in general the heavier compounds are at levels about 100 times lower than that of benzene.

Although the list of compounds from Table 7.1.3 does not continue beyond ethynylpyrene (MW = 226.28), heavier PAHs also are formed in the pyrolysis of hydrocarbons with a small molecule (C<sub>1</sub> to C<sub>5</sub>). The level of these heavier compounds can be extremely low, beyond the detection capability of the analytical procedure (GC/MS in this case) [50]. The knowledge of the formation of PAHs in the pyrolysis of hydrocarbons at temperatures above 900 °C is important for a number of industrial processes, considering the implications of PAHs in health and environmental issues.

Pyrolysis of propane in the presence of other hydrocarbons also has been studied [54]. This type of information is particularly important for industrial processes where it is uncommon to pyrolyze a pure

TABLE 7.1.3. Compounds above seven carbon atoms in the molecule detected during propane pyrolysis between 1173 K and 1298 K in a CVI experiment [53]

Name	Formula	Name	Formula
Phenylacetylene	C <sub>8</sub> H <sub>6</sub>	1,1-Dimethylindene	C <sub>11</sub> H <sub>12</sub>
Styrene	C <sub>8</sub> H <sub>8</sub>	1,7-Dimethylindene	C <sub>11</sub> H <sub>12</sub>
o-Xylene	C <sub>8</sub> H <sub>10</sub>	1-Ethynynaphthalene	C <sub>12</sub> H <sub>8</sub>
p-Xylene	C <sub>8</sub> H <sub>10</sub>	Acenaphthylene	C <sub>12</sub> H <sub>8</sub>
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	1-Ethenynaphthalene	C <sub>12</sub> H <sub>10</sub>
3,4-Dimethyl-1,5-hexadiene	C <sub>8</sub> H <sub>14</sub>	2-Ethenynaphthalene	C <sub>12</sub> H <sub>10</sub>
2-Ethenyl-1-methylbenzene	C <sub>9</sub> H <sub>8</sub>	Biphenyl	C <sub>12</sub> H <sub>10</sub>
3-Ethenyl-1-methylbenzene	C <sub>9</sub> H <sub>8</sub>	1,3-Dimethylnaphthalene	C <sub>12</sub> H <sub>12</sub>
4-Ethenyl-1-methylbenzene	C <sub>9</sub> H <sub>8</sub>	Ethynaphthalene	C <sub>12</sub> H <sub>12</sub>
Prop-2-ynylbenzene	C <sub>9</sub> H <sub>8</sub>	1-Methyl-8-vinylnaphthalene	C <sub>13</sub> H <sub>12</sub>
Indene	C <sub>9</sub> H <sub>8</sub>	Methylacenaphthene	C <sub>13</sub> H <sub>12</sub>
Prop-2-enylbenzene	C <sub>9</sub> H <sub>10</sub>	Benzylbenzene	C <sub>13</sub> H <sub>12</sub>
2-Methylstyrene	C <sub>9</sub> H <sub>10</sub>	4-Methyl-1-phenylbenzene	C <sub>13</sub> H <sub>12</sub>
(1-Methylvinyl)benzene	C <sub>9</sub> H <sub>10</sub>	Propylnaphthalene	C <sub>13</sub> H <sub>14</sub>
Indane	C <sub>9</sub> H <sub>10</sub>	5-Ethynylacenaphthylene	C <sub>14</sub> H <sub>8</sub>
(1-Ethynylvinyl)benzene	C <sub>10</sub> H <sub>8</sub>	5-Ethenylacenaphthylene	C <sub>14</sub> H <sub>10</sub>
Naphthalene	C <sub>10</sub> H <sub>8</sub>	Anthracene	C <sub>14</sub> H <sub>10</sub>
2-Ethyl-1-ethenylbenzene	C <sub>10</sub> H <sub>10</sub>	Phenanthrene	C <sub>14</sub> H <sub>10</sub>
4-Ethyl-1-ethenylbenzene	C <sub>10</sub> H <sub>10</sub>	Stilbene	C <sub>14</sub> H <sub>12</sub>
Methylindene	C <sub>10</sub> H <sub>10</sub>	Bibenzyl	C <sub>14</sub> H <sub>14</sub>
7-Methylindene	C <sub>10</sub> H <sub>10</sub>	Methylantracene	C <sub>15</sub> H <sub>12</sub>
Bicyclopentyl-2,2',4,4'-tetraene	C <sub>10</sub> H <sub>10</sub>	4-Methylphenanthrene	C <sub>15</sub> H <sub>12</sub>
Ethynylindene	C <sub>11</sub> H <sub>8</sub>	Ethynylantracene	C <sub>16</sub> H <sub>10</sub>
7-Ethynylindene	C <sub>11</sub> H <sub>8</sub>	Pyrene	C <sub>16</sub> H <sub>10</sub>
1-Methylnaphthalene	C <sub>11</sub> H <sub>10</sub>	Methylpyrene	C <sub>17</sub> H <sub>12</sub>
Cyclopenta-2,4-dienylbenzene	C <sub>11</sub> H <sub>10</sub>	Ethynylpyrene	C <sub>18</sub> H <sub>10</sub>

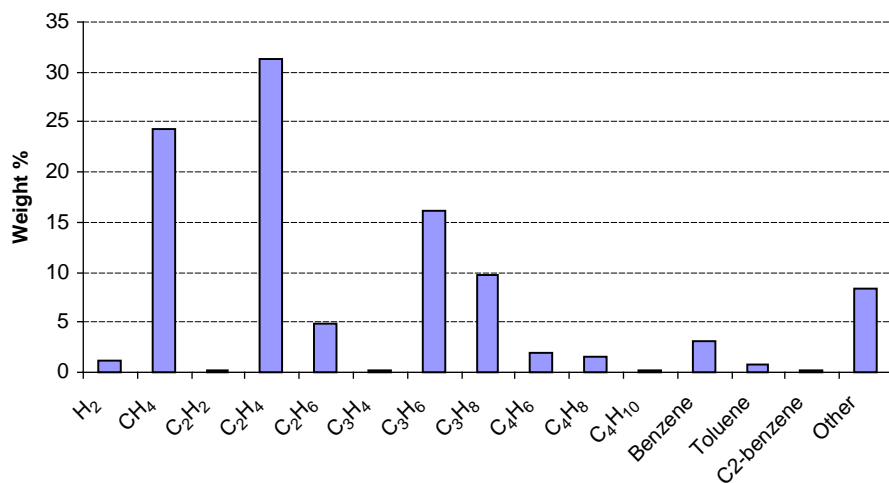


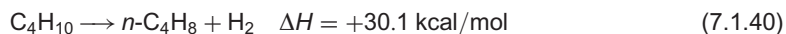
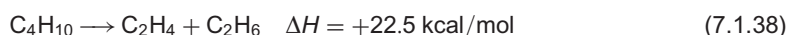
FIGURE 7.1.6. Composition of a pyrolysate obtained from 86.4% propane (in mixture with other small hydrocarbons) at 650 °C in an industrial reactor [54].

compound. For example, pyrolysis of a mixture of 86.4% propane with 0.15% ethane, 4.34% propene, 5.72% *n*-butane, 2.51% isobutane, and 0.85% butene at 650 °C in an industrial reactor with a residence time of 0.8 s leads to a mixture of products, as indicated in Figure 7.1.6.

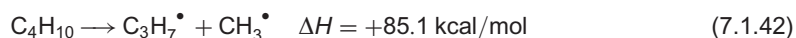
Similar to the case of methane and ethane, oxidative pyrolysis plays an important role in the first stages of propane burning [55–57]. The reactions in propane burning are similar to those previously discussed for methane and ethane. Several studies on catalytic pyrolysis of propane are reported in the literature [27,58].

### Butane and isobutane

Butane pyrolysis at temperatures between 700 °C and 840 °C generates mainly propylene, ethylene, methane, and hydrogen, with small quantities of ethane and traces of butenes (isomers) and carbon [59,60]. The main reactions taking place during pyrolysis are the following:



The relative importance of the individual reactions 7.1.37–7.1.40 in the initial stages of decomposition of butane around 500 °C were estimated to be 71%, 21%, 8%, and less than 1%, respectively [61]. A free radical decomposition mechanism is involved in butane pyrolysis similar to those from the pyrolysis of methane, ethane, and propane. Two main reactions occur in the initiation step:



These reactions continue with the generation of other free radicals due to numerous propagation reactions. Among the newly formed free radicals are  $\text{H}^\bullet$ ,  $\text{CH}_3^\bullet$ ,  $\text{C}_4\text{H}_9^\bullet$ , and, at a lower extent, numerous other ones similar to those indicated for propane pyrolysis in Table 7.1.1. The composition of pyrolysates depends on temperature, time of reaction, and pressure of the reacting gas. Although involving two initiation steps, the overall decomposition reaction of butane can be approximated to have a first order kinetics. The measurements performed in the temperature interval 720–840 °C in a stainless steel reactor gave for Arrhenius equation  $A = 5.68 \times 10^{11} \text{ s}^{-1}$  and  $E^\ddagger = 60.35 \text{ kcal/mol}$  [59] and for the measurements in a quartz reactor gave  $A = 5.10 \times 10^{12} \text{ s}^{-1}$  and  $E^\ddagger = 58.7 \text{ kcal/mol}$  [62]. The difference shows the importance of the reactions at the reactor surface during pyrolysis of butane (and other gaseous hydrocarbons). In other studies the reaction kinetics was approximated as having a reaction order of 1.5 [63,64]. The estimated values for the activation energy  $E^\ddagger$  in Arrhenius equation was similar to that for first order reaction, but different values (and units) were described for the frequency factor. The decrease in the initial molar % of butane as a function of temperature at four different heating times is given in Figure 7.1.7.

The composition of the reaction products also varies with time and temperature. For a heating time of 0.5 s, the mole % in the reaction products as a function of temperature is shown in Figure 7.1.8. As seen from this figure, the mole proportion of propylene decreases when the temperature increases, while the proportion of ethylene increases. The hydrogen formation has an initial decrease and then an increase at higher temperatures [59].

The presence of higher molecular weight compounds begin to be noticed in *n*-butane pyrolysate at 725 °C and exposure time of about 5 s, when *n*-butane conversion is greater than 95%. Similar to all hydrocarbons, in the final stage of thermal decomposition, the formation of carbon (soot) is typical.

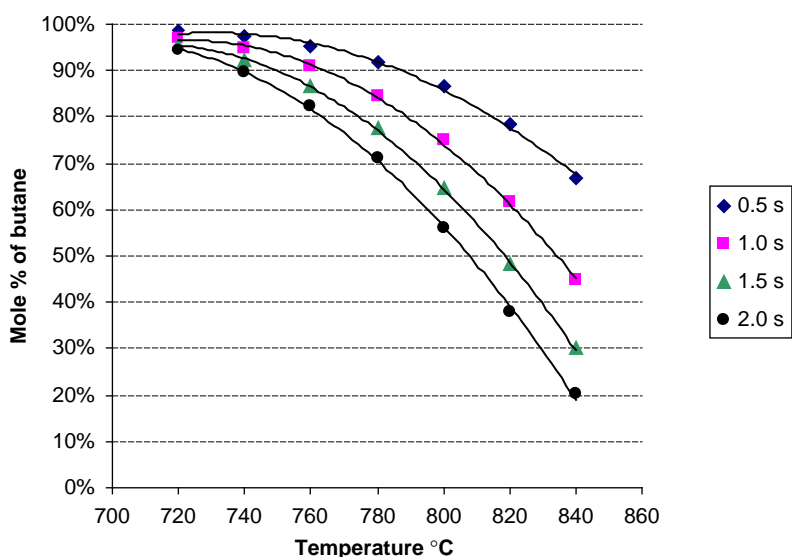


FIGURE 7.1.7. Variation in the molar percent of remaining butane as a function of temperature at four different heating times.

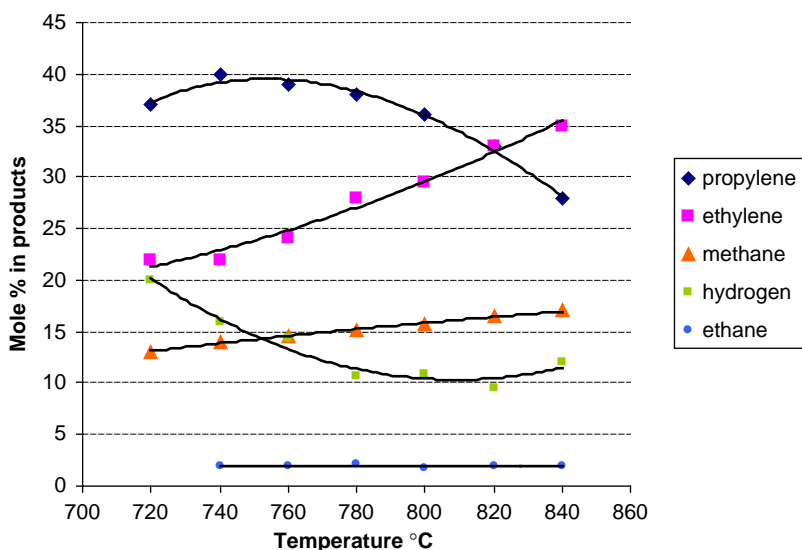
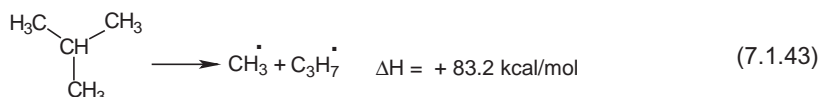


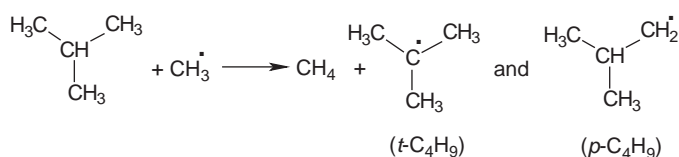
FIGURE 7.1.8. Molar percent of several reaction products (excluding butane) in butane pyrolysate as a function of temperature and a heating time of 0.5 s.

Pyrolysis of butane is strongly influenced by the presence of traces of oxygen (between 5 ppm and 200 ppm) [63] and by the nature of the walls of the reaction vessel, which may have catalytic effects. The increase in the oxygen concentration up to 200 ppm decreases the rate of butane pyrolysis, probably as a result of the consumption of free radicals generated during the initiation step. Further increase in the oxygen content leads to a slight increase in the rate of decomposition [61]. The presence of oxygen traces does not affect significantly the ratios of methane, ethane, ethylene, and propylene. However, with the increase in the oxygen content, increased proportions of 1-butene, 2-butenes (*cis* and *trans*), 1,3-butadiene, and water are detected.

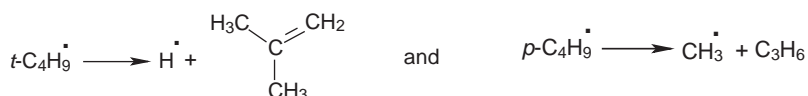
Pyrolysis of isobutane follows the same rules as that of butane. The initiation reaction for pyrolysis is basically the following:



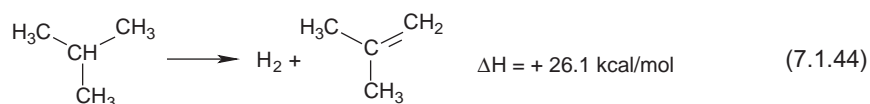
Hydrogen atoms formation is considerably more endothermic and therefore, less likely to occur (primary C—H bond energy of 98.2 kcal/mol and tertiary C—H bond energy of 96.5 kcal/mol, as seen in Table 3.1.2). The initial free radicals will further generate other free radicals in various propagation steps. The reaction of  $\text{CH}_3^\bullet$  with isobutane can generate two types of isobutyl radicals with the unpaired electron at the primary carbon ( $p\text{-C}_4\text{H}_9^\bullet$ ) and at the tertiary carbon ( $t\text{-C}_4\text{H}_9^\bullet$ ), as shown below:



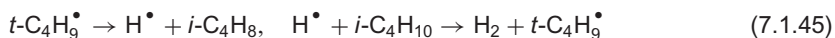
Further reactions with the formation of hydrogen atoms and of new methyl radicals take place as shown below:



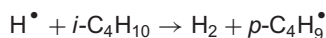
As a result of free radical formation and propagation processes, hydrogen, isobutene, methane, propene, and ethylene, as well as other small molecules, are formed. The main reaction, accounting for 75% of pyrolysate at 470 °C and at 100 Torr, can be considered the following [65,66]:



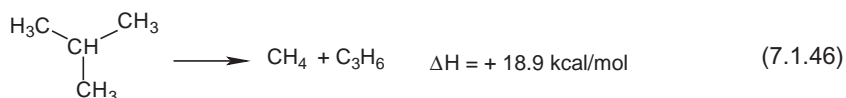
This reaction can be considered the result of the following sequence:



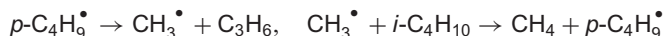
(where *i*- indicates iso). The free hydrogen atoms involved in reaction 7.1.45 also are able to generate  $p\text{-C}_4\text{H}_9^\bullet$  as shown below:



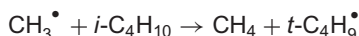
Another important reaction (accounting for 25% of pyrolysate at 470 °C and at 100 Torr) is the following:



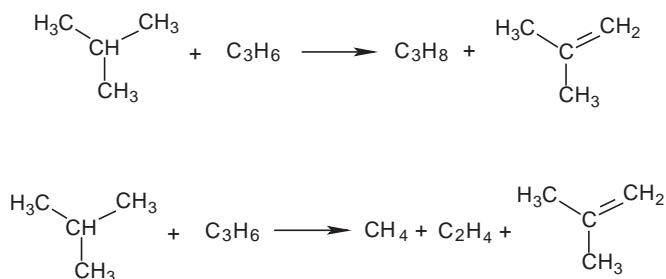
This reaction can be considered the result of the following sequence:



Besides  $p\text{-C}_4\text{H}_9^\bullet$ , formation of  $t\text{-C}_4\text{H}_9^\bullet$  takes place in the interaction with methyl radicals:



Other reactions take place as a result of propagation process. The overall result is the formation of various small molecules such as propane, methane, and ethylene, as shown in the following two examples:



The intermediate steps of these reactions involve free radicals. The termination reactions also involve free radicals that combine between themselves with or without disproportionation.

In comparing the decomposition of isobutane with that of butane, it can be observed that isobutane is more reactive than  $n$ -butane at similar experimental conditions. The pyrolysis of isobutane forms considerably less  $\text{C}_2$  species than  $n$ -butane pyrolysis. This is expected because the branched nature of isobutane does not allow C–C  $\beta$ -scission from the parent isomer to form  $\text{C}_2$  species. The formation of compounds with higher molecular weight during isobutane pyrolysis does not begin below  $750^\circ\text{C}$ .

### Other low-molecular-weight saturated hydrocarbons

The pyrolysis of hydrocarbons with 5–11 carbon atoms has received less attention than pyrolysis of short-chain hydrocarbons [67,68]. Several experimental studies showed that normal hydrocarbons have both similarities but also some differences compared to that of branched ones [66,69,70]. The branched hydrocarbons decompose at slightly lower temperatures, the initiation reaction for these compounds being 2–4 kcal/mol less endothermic.

A typical study on normal hydrocarbons has been performed on  $n$ -hexane [67]. The main reaction products of hexane pyrolysis are ethylene, methane, propene, ethane, 1-butene, 1-pentene, and hydrogen. The model reactions used successfully to model the results regarding the decomposition of hexane around  $420^\circ\text{C}$  and 100 Torr at low conversion (beginning of the decomposition) and their parameters in Arrhenius equation are shown in Table 7.1.4 [67].

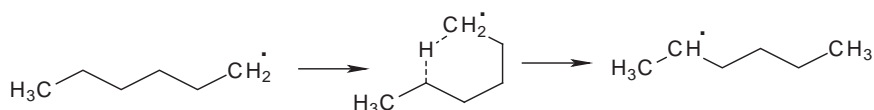
The reactions from Table 7.1.4 represent only the main processes involved in the initial step of hexane pyrolysis. As seen from the list of reactions in this table, the mechanisms of the pyrolysis process involve free radicals, similar to the pyrolysis of shorter-chain hydrocarbons. No evidence was found that a  $\beta$ -elimination with concerted mechanism would take place in hexane pyrolysis. Isomerization reactions of the radicals are not listed in Table 7.1.4 although they are known to occur, since they take place after the initial step of radical formation. A typical “back biting” radical



TABLE 7.1.4. Model reactions for hexane initial phases of pyrolysis [67] and the corresponding Arrhenius parameters

Reaction	A	E <sup>‡</sup> (kcal/mol)
Initiation reaction		
$C_6H_{14} \rightarrow C_2H_5^{\bullet} + C_4H_9^{\bullet}$	$1.58 \times 10^{17}$	81.3
$C_6H_{14} \rightarrow C_3H_7^{\bullet} + C_3H_7^{\bullet}$	$3.61 \times 10^{16}$	81.9
$C_6H_{14} \rightarrow CH_3^{\bullet} + C_5H_{11}^{\bullet}$	$1.58 \times 10^{17}$	85.4
H <sup>•</sup> abstractions by radicals		
$CH_3^{\bullet} + C_6H_{14} \rightarrow CH_4 + CH_3CH_2CH_2CH_2CH_2CH_2^{\bullet}$	$3.98 \times 10^{11}$	11.4
$CH_3^{\bullet} + C_6H_{14} \rightarrow CH_4 + CH_3CH^{\bullet}CH_2CH_2CH_2CH_3$	$5.62 \times 10^{11}$	9.6
$CH_3^{\bullet} + C_6H_{14} \rightarrow CH_4 + CH_3CH_2CH^{\bullet}CH_2CH_2CH_3$	$3.93 \times 10^{11}$	9.6
$C_2H_5^{\bullet} + C_6H_{14} \rightarrow C_2H_6 + CH_3CH_2CH_2CH_2CH_2CH_2^{\bullet}$	$3.16 \times 10^{11}$	12.3
$C_2H_5^{\bullet} + C_6H_{14} \rightarrow C_2H_6 + CH_3CH^{\bullet}CH_2CH_2CH_2CH_3$	$1.00 \times 10^{11}$	10.4
H <sup>•</sup> abstractions by radicals		
$C_2H_5^{\bullet} + C_6H_{14} \rightarrow C_2H_6 + CH_3CH_2CH^{\bullet}CH_2CH_2CH_3$	$1.57 \times 10^{11}$	10.4
$H^{\bullet} + C_6H_{14} \rightarrow H_2 + CH_3CH^{\bullet}CH_2CH_2CH_2CH_3$	$5.01 \times 10^{11}$	7.1
$H^{\bullet} + C_6H_{14} \rightarrow H_2 + CH_3CH_2CH^{\bullet}CH_2CH_2CH_3$	$5.01 \times 10^{11}$	7.1
$CH_3^{\bullet} + C_3H_6 \rightarrow CH_4 + C_3H_5^{\bullet}$	$1.26 \times 10^{11}$	8.2
$H^{\bullet} + C_3H_6 \rightarrow H_2 + C_3H_5^{\bullet}$	$1.0 \times 10^{14}$	3.5
Radical decompositions (with isomerization)		
$CH_3CH_2CH_2CH_2CH_2CH_2^{\bullet} \rightarrow C_2H_4 + C_4H_9^{\bullet}$	$2.51 \times 10^{13}$	28.8
$CH_3CH^{\bullet}CH_2CH_2CH_2CH_3 \rightarrow C_3H_6 + C_3H_7^{\bullet}$	$1.58 \times 10^{13}$	28.3
$CH_3CH_2CH^{\bullet}CH_2CH_2CH_3 \rightarrow C_4H_8 + C_2H_5^{\bullet}$	$1.25 \times 10^{13}$	29.1
$CH_3CH_2CH^{\bullet}CH_2CH_2CH_3 \rightarrow C_5H_{10} + CH_3^{\bullet}$	$5.39 \times 10^{13}$	33.0
$C_2H_5^{\bullet} \rightarrow C_2H_4 + H^{\bullet}$	$3.98 \times 10^{13}$	40.3
$C_3H_7^{\bullet} \rightarrow C_3H_6 + H^{\bullet}$	$7.54 \times 10^{13}$	38.6
$C_3H_7^{\bullet} \rightarrow C_2H_4 + CH_3^{\bullet}$	$1.58 \times 10^{13}$	32.7
$C_4H_9^{\bullet} \rightarrow C_2H_4 + C_2H_5^{\bullet}$	$1.41 \times 10^{13}$	28.75
$C_4H_9^{\bullet} \rightarrow C_3H_6 + CH_3^{\bullet}$	$1.0 \times 10^{15}$	34.5
Termination reactions		
$CH_3^{\bullet} + CH_3^{\bullet} \rightarrow C_2H_6$	$k = 2.51 \times 10^{13}$	0
$CH_3^{\bullet} + C_2H_5^{\bullet} \rightarrow C_3H_8$	$k = 2.00 \times 10^{13}$	0
$CH_3^{\bullet} + C_3H_7^{\bullet} \rightarrow C_4H_{10}$	$k = 2.00 \times 10^{13}$	0
$C_2H_5^{\bullet} + C_2H_5^{\bullet} \rightarrow C_4H_{10}$	$k = 3.89 \times 10^{12}$	0
$C_2H_5^{\bullet} + C_3H_5^{\bullet} \rightarrow C_5H_{10}$	$k = 1.00 \times 10^{13}$	0
$C_2H_5^{\bullet} + C_3H_7^{\bullet} \rightarrow C_5H_{12}$	$k = 7.49 \times 10^{12}$	0
Termination with disproportionation		
$H^{\bullet} + C_2H_5^{\bullet} \rightarrow C_2H_4 + H_2$	$k = 2.0 \times 10^{12}$	0
$CH_3^{\bullet} + C_3H_7^{\bullet} \rightarrow C_2H_4 + C_2H_6$		0
$C_2H_5^{\bullet} + C_2H_5^{\bullet} \rightarrow C_2H_4 + C_2H_6$		0
$C_2H_5^{\bullet} + C_3H_7^{\bullet} \rightarrow C_2H_4 + C_3H_8$		0
$C_2H_5^{\bullet} + C_3H_7^{\bullet} \rightarrow C_2H_6 + C_3H_6$		0

isomerization is shown below:



The participation of longer radicals (such as butyl, pentyl, and hexyl) in the termination reactions that lead to branched hydrocarbon formation is not shown in Table 7.1.4 since it does not have an important role in the formation of pyrolysis products. However, such reactions do occur and lead to a complex outcome of the pyrolytic process. The initial set of reactions in hexane pyrolysis is followed by a secondary set of reactions. This secondary set of reactions consists of radical isomerizations and further pyrolysis of the compounds formed in the first step. For example, the alkenes formed in the first step can undergo unimolecular initiations with the formation of allyl type radicals. Other reactions such as additions and radical combinations with the formation of hydrocarbons with higher number of carbons are possible. Longer pyrolysis times and higher temperatures lead to further reactions with formation of molecules with higher molecular weight and finally to carbon (soot). The modeling of pyrolysis using the reactions from Table 7.1.4 is able to predict a self-inhibiting process that results in a slower rate of small molecules production (e.g.,  $\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ) compared to the initial rate. This process is probably caused by the transformation of more active radicals ( $\text{H}^\bullet$ ,  $\text{CH}_3^\bullet$ ,  $\text{C}_2\text{H}_5^\bullet$ ,  $\text{C}_3\text{H}_7^\bullet$ ) generated in the initial phase into many allyl radicals ( $\text{C}_3\text{H}_5^\bullet$ ) that are stabilized by resonance and are less reactive.

Pyrolysis of 3-methylpentane generates mainly methane, ethane, 2-butane, 2-methyl-1-butene, ethylene, and propylene, with smaller amounts of 2-pentene, 1-butene, and hydrogen [69]. The main pyrolysis steps including some parameters in Arrhenius equation for 420 °C and 100 Torr as used in computer modeling are given in Table 7.1.5.

Except for additional complexity caused by the presence of more isomers, the pyrolysis of 3-methylpentane is very similar to that of hexane. The dissociation energy for the C–H bond typically decreases slightly from primary carbons (98.2 kcal/mol) to secondary (94.2 kcal/mol) and further to tertiary ones (91.1 kcal/mol). The dissociation energy for the C–C bond slightly decreases in the same direction, as seen in Table 3.1.2. This would indicate that branched hydrocarbons might start decomposing at slightly lower temperatures as compared to linear ones. Since the pyrolysis process involves a large number of reactions and the outcome of the process depends on numerous other reactions, the differences that can appear in the initiation reactions may be overcome by other reactions. The result is that the pyrolysis products of branched hydrocarbons do not differ significantly from that of the linear ones, only the reaction rates being somewhat different [71]. Only in instances where the initial pyrolytic process is the determining step, are some differences noticeable. For example, in the combustion of hydrocarbons, it was demonstrated that the initial formation of free radicals due to pyrolysis plays an important role. For this reason, the difference between linear and branched hydrocarbons in their initial pyrolysis step of combustion plays an important role in the value of the octane rating [72]. The octane rating is a measure of the autoignition resistance of gasoline (and other fuels) in a spark-ignition combustion engine. This autoignition is related to the activation energy of the molecules of the carburant. The whole structure of the molecule of the carburant determines the activation energy; a simple assessment based on branched or not branched structure is sufficient for a conclusion [73]. The octane rating usually is done with a research octane number (RON), which is measured with a special test engine with variable compression ratio. The RON value for 2,2,4-trimethylpentane (isooctane) is 100, and that of *n*-heptane is 0 (*n*-octane has a RON value of –10). The RON value is, as expected, related to the activation energy of the initial pyrolytic reactions of the gasoline components. Evaluation of RON values and their relation to the pyrolysis/oxidation process for *n*-heptane (RON = 0) and for isooctane (RON = 100) has been reported frequently in the literature [74,75].

In addition to simple pyrolysis, other pyrolytic conditions were studied, particularly for pentanes and hexanes. These include pyrolysis at very high pressure [76], pyrolysis over catalysts [77,78], pyrolysis in the presence of oxygen [79], and pyrolysis in the presence of hydrogen [80,81]. Various studies were performed to study the combustion of linear and branched hydrocarbons [82,83].

TABLE 7.1.5. Model reactions for 3-methylpentane ( $i\text{-C}_6\text{H}_{14}$ ) initial phases of pyrolysis [69] and the corresponding Arrhenius parameters

Reaction	A	$E^\ddagger$ (kcal/mol)
Initiation reaction		
$i\text{-C}_6\text{H}_{14} \rightarrow \text{CH}_3^\bullet + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2^\bullet$	$6.3 \times 10^{16}$	85.4
$i\text{-C}_6\text{H}_{14} \rightarrow \text{CH}_3^\bullet + \text{CH}_3\text{CH}_2\text{CH}^\bullet\text{CH}_2\text{CH}_3$	$1.0 \times 10^{17}$	82.9
$i\text{-C}_6\text{H}_{14} \rightarrow \text{C}_2\text{H}_5^\bullet + \text{CH}_3\text{CH}^\bullet\text{CH}_2\text{CH}_3$	$6.3 \times 10^{16}$	79.2
$i\text{-C}_6\text{H}_{14} \rightarrow \text{H}^\bullet + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2^\bullet$	$2.5 \times 10^{13}$	78.0
$\text{H}^\bullet$ abstractions by radicals		
$\text{H}^\bullet + i\text{-C}_6\text{H}_{14} \rightarrow \text{H}_2 + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2^\bullet$	$1.25 \times 10^{14}$	9.7
$\text{H}^\bullet + i\text{-C}_6\text{H}_{14} \rightarrow \text{H}_2 + \text{CH}_3\text{CH}^\bullet\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	$5.01 \times 10^{14}$	7.1
$\text{H}^\bullet + i\text{-C}_6\text{H}_{14} \rightarrow \text{H}_2 + \text{CH}_3\text{CH}_2\text{C}^\bullet(\text{CH}_3)\text{CH}_2\text{CH}_3$	$5.01 \times 10^{13}$	7.1
$\text{H}^\bullet + i\text{-C}_6\text{H}_{14} \rightarrow \text{H}_2 + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2^\bullet)\text{CH}_2\text{CH}_3$	$2.5 \times 10^{13}$	7.1
$\text{CH}_3^\bullet + i\text{-C}_6\text{H}_{14} \rightarrow \text{CH}_4 + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2^\bullet$	$3.98 \times 10^{11}$	11.4
$\text{CH}_3^\bullet + i\text{-C}_6\text{H}_{14} \rightarrow \text{CH}_4 + \text{CH}_3\text{CH}^\bullet\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	$5.62 \times 10^{11}$	9.6
$\text{CH}_3^\bullet + i\text{-C}_6\text{H}_{14} \rightarrow \text{CH}_4 + \text{CH}_3\text{CH}_2\text{C}^\bullet(\text{CH}_3)\text{CH}_2\text{CH}_3$	$3.93 \times 10^{11}$	9.6
$\text{CH}_3^\bullet + i\text{-C}_6\text{H}_{14} \rightarrow \text{CH}_4 + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2^\bullet)\text{CH}_2\text{CH}_3$	$3.98 \times 10^{11}$	11.4
$\text{C}_2\text{H}_5^\bullet + i\text{-C}_6\text{H}_{14} \rightarrow \text{C}_2\text{H}_6 + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2^\bullet$	$3.16 \times 10^{11}$	12.3
$\text{C}_2\text{H}_5^\bullet + i\text{-C}_6\text{H}_{14} \rightarrow \text{C}_2\text{H}_6 + \text{CH}_3\text{CH}^\bullet\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	$1.00 \times 10^{11}$	10.4
$\text{C}_2\text{H}_5^\bullet + i\text{-C}_6\text{H}_{14} \rightarrow \text{C}_2\text{H}_6 + \text{CH}_3\text{CH}_2\text{C}^\bullet(\text{CH}_3)\text{CH}_2\text{CH}_3$	$1.00 \times 10^{11}$	10.4
$\text{C}_2\text{H}_5^\bullet + i\text{-C}_6\text{H}_{14} \rightarrow \text{C}_2\text{H}_6 + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2^\bullet)\text{CH}_2\text{CH}_3$	$3.16 \times 10^{11}$	12.3
$\text{CH}_3\text{CH}^\bullet\text{CH}_2\text{CH}_3 + i\text{-C}_6\text{H}_{14} \rightarrow n\text{-C}_4\text{H}_{10} + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2^\bullet$	$1.00 \times 10^{11}$	12.9
$\text{CH}_3\text{CH}^\bullet\text{CH}_2\text{CH}_3 + i\text{-C}_6\text{H}_{14} \rightarrow n\text{-C}_4\text{H}_{10} + \text{CH}_3\text{CH}^\bullet\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	$1.00 \times 10^{11}$	10.4
$\text{CH}_3\text{CH}^\bullet\text{CH}_2\text{CH}_3 + i\text{-C}_6\text{H}_{14} \rightarrow n\text{-C}_4\text{H}_{10} + \text{CH}_3\text{CH}_2\text{C}^\bullet(\text{CH}_3)\text{CH}_2\text{CH}_3$	$1.00 \times 10^{11}$	10.4
$\text{CH}_3\text{CH}^\bullet\text{CH}_2\text{CH}_3 + i\text{-C}_6\text{H}_{14} \rightarrow n\text{-C}_4\text{H}_{10} + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2^\bullet)\text{CH}_2\text{CH}_3$	$1.00 \times 10^{11}$	12.9
$\text{CH}_3\text{CH}^\bullet\text{CH}_3 + \text{C}_3\text{H}_6 \rightarrow \text{C}_3\text{H}_8 + \text{CH}_2^\bullet\text{CH}=\text{CH}_2$	$1.00 \times 10^{11}$	10.8
$\text{CH}_3\text{CH}_2^\bullet + \text{C}_3\text{H}_6 \rightarrow \text{C}_2\text{H}_6 + \text{CH}_2^\bullet\text{CH}=\text{CH}_2$	$4.00 \times 10^{11}$	8.3
$\text{CH}_3^\bullet + \text{C}_3\text{H}_6 \rightarrow \text{CH}_4 + \text{CH}_2^\bullet\text{CH}=\text{CH}_2$	$1.58 \times 10^{11}$	8.8
$\text{H}^\bullet + \text{C}_3\text{H}_6 \rightarrow \text{H}_2 + \text{CH}_2^\bullet\text{CH}=\text{CH}_2$	$1.00 \times 10^{14}$	3.5
Radical additions		
$\text{H}^\bullet + \text{C}_2\text{H}_4 \rightarrow \text{CH}_3\text{CH}_2^\bullet$	$1.0 \times 10^{13}$	2.6
$\text{H}^\bullet + \text{C}_3\text{H}_6 \rightarrow \text{CH}_3\text{CH}^\bullet\text{CH}_3$	$7.9 \times 10^{12}$	1.2
Radical decompositions		
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2^\bullet \rightarrow \text{CH}_3\text{CH}^\bullet\text{CH}_2\text{CH}_3 + \text{C}_2\text{H}_4$	$3.98 \times 10^{12}$	26.2
$\text{CH}_3\text{CH}^\bullet\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2^\bullet + \text{CH}_3\text{CH}=\text{CHCH}_3$	$5.00 \times 10^{12}$	29.1
$\text{CH}_3\text{CH}_2\text{C}^\bullet(\text{CH}_3)\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3^\bullet + \text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	$7.94 \times 10^{13}$	33.0
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2^\bullet)\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2^\bullet + \text{CH}_2=\text{CHCH}_2\text{CH}_3$	$1.25 \times 10^{13}$	29.5
$\text{CH}_3\text{CH}^\bullet\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3^\bullet + \text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$	$7.94 \times 10^{13}$	33.0
$\text{CH}_3\text{CH}^\bullet\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3^\bullet + \text{C}_3\text{H}_6$	$1.33 \times 10^{14}$	33.2
$\text{CH}_3\text{CH}_2^\bullet \rightarrow \text{H}^\bullet + \text{C}_2\text{H}_4$	$3.98 \times 10^{13}$	40.5
$\text{CH}_3\text{CH}^\bullet\text{CH}_2\text{CH}_3 \rightarrow \text{H}^\bullet + \text{CH}_2=\text{CHCH}_2\text{CH}_3$	$1.99 \times 10^{13}$	40.4
$\text{CH}_3\text{CH}^\bullet\text{CH}_2\text{CH}_3 \rightarrow \text{H}^\bullet + \text{CH}_3\text{CH}=\text{CHCH}_3$	$5.01 \times 10^{12}$	37.9
$\text{CH}_3\text{CH}^\bullet\text{CH}_3 \rightarrow \text{H}^\bullet + \text{C}_3\text{H}_6$	$7.90 \times 10^{13}$	40.4
Terminations		
$\text{H}^\bullet + \text{CH}_3^\bullet \rightarrow \text{CH}_4$	$1.99 \times 10^{14}$	0

(Continued)



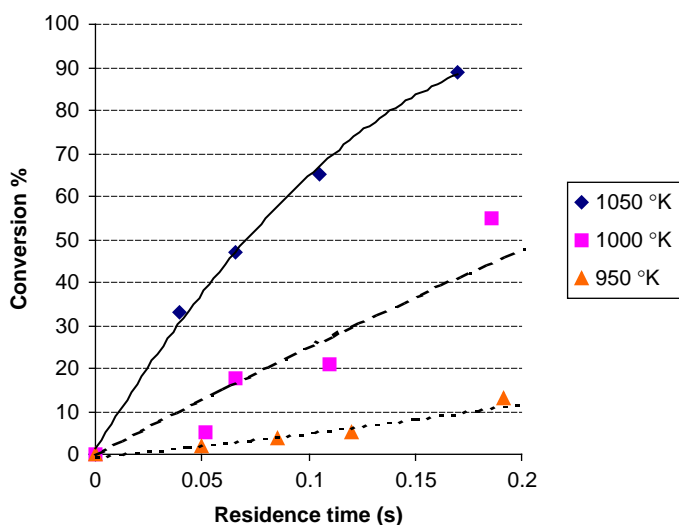


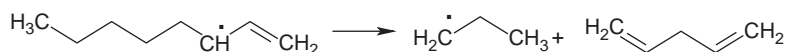
FIGURE 7.1.9. Conversion of *n*-dodecane as a function of residence time in a pyrolyzer, at three different temperatures [86].

Termination reactions similar to those shown in Table 7.1.4 for 3-methylpentane take place with the formation of linear and branched hydrocarbons.

After the first stage of reactions, a secondary stage follows. This is similar to that noticed for hexane but has even more complexity. Unimolecular initiations from alkenes previously formed lead to allyl type radicals. An increase in the initial number of carbons of the hydrocarbon is possible. Some reaction products can undergo additions of the type:

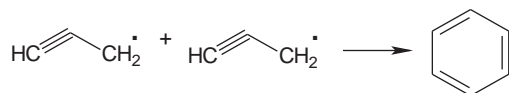


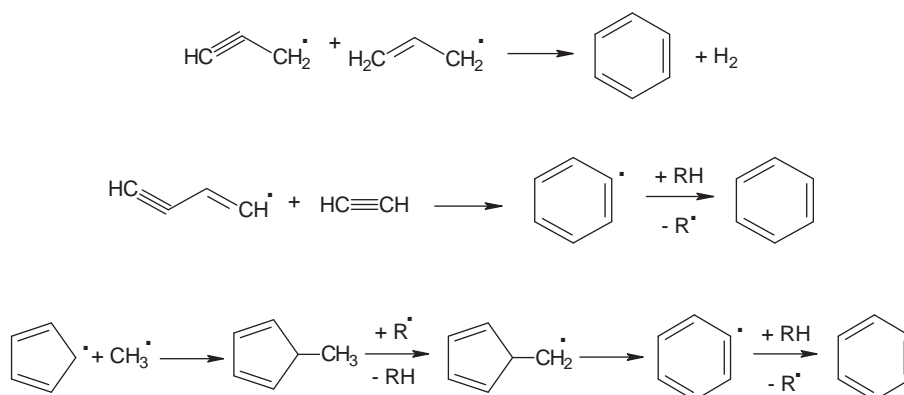
The hydrogen abstraction, “back biting,” and  $\beta$ -scission of the radicals can generate various alkenes, dienes, etc. Formation of 1,4-pentadiene, for example, can take place by the following type of reaction:



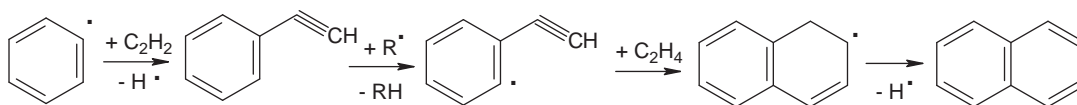
Some alkenes may undergo retro-ene reactions with the formation of two shorter alkenes.

The formation of compounds with triple bonds such as acetylene, propyne, and vinylacetylene, and of cyclopentadiene, methycyclopentadiene, etc., begins at long heating times and/or high temperatures. These compounds can react further with the formation of aromatic hydrocarbons. As an example, formation of benzene can take place following different pathways, as shown below:

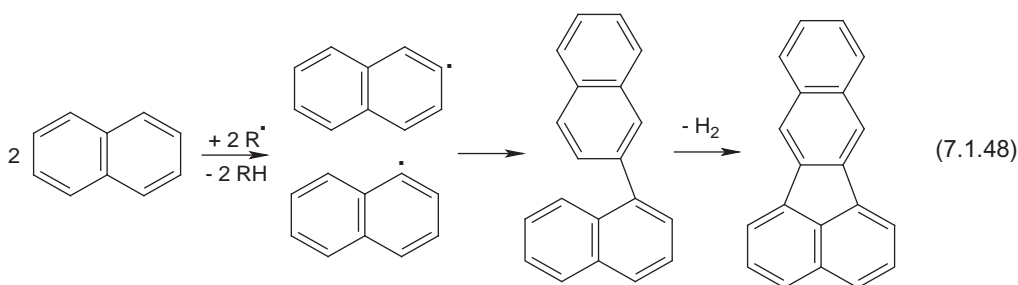




Phenyl radicals continue to interact among themselves or with different other pyrolysis components and larger molecules are formed. The formation of naphthalene is shown below as an example starting with phenyl and acetylene in a so-called HACA reaction (hydrogen abstraction acetylene addition):



Naphthalene can react further to form, for example, benzo[k]fluoranthene, as shown in the following reactions:

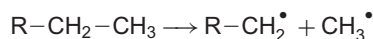


Benzo[k]fluoranthene was not reported in *n*-dodecane pyrolysate, only PAHs with molecular weight up to 202 (pyrene) being detected. However, heavier compounds were formed, but they were at too low levels compared to the detection limit of the analyses. Formation of PAHs in the oxidative process and during pyrolysis of alkanes has been studied extensively and reported in the literature [88,89].

### Higher molecular weight alkanes

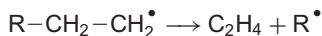
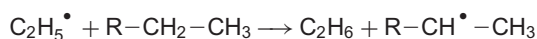
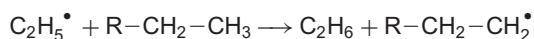
Pyrolysis of higher molecular weight alkanes has important practical applications related to petroleum cracking. The process has been studied on pure compounds and on mixtures, at different temperatures, pressures, and conversion rates. The pyrolysis reactions occur by mechanisms similar to those of alkanes with smaller molecular weight, i.e., mainly by radicalic mechanisms. In later stages of the pyrolysis, other reactions such as retro-ene and Diels–Alder condensations may occur, but those are not the dominant processes in the initial stages (and Diels–Alder reactions are not favored by the increase in temperature). The initiation reaction is typically the scission of a C–C bond in different

positions along the molecule carbon chain with the formation of free radicals, as shown below for a 1,2-scission:



Since the initiation reactions are typically more endothermic than propagations and terminations, the initiation step plays a more important role in determining the composition of the pyrolysate when temperature is increased. The increased role of initiation (e.g., due to a higher pyrolysis temperature) diminishes the role of propagation reactions, and the effect on composition is the presence of more products generated by termination reactions and less of those resulting from propagations.

The formation of free radicals is followed by complex propagation reactions, the most common ones being the formation of new free radicals and of alkenes by hydrogen abstractions and radical decomposition by  $\beta$ -scissions. Examples of such reactions with formation of ethylene and ethane are shown below:



The hydrogen abstraction reactions are favored for tertiary carbons, followed by secondary carbons as compared to primary ones. The activation energy for a  $\text{H}^\bullet$  abstraction is usually 4 kcal/mol lower for a tertiary carbon and 2 kcal/mol lower for a secondary carbon as compared to a primary one (see Table 7.1.5). Because these energetic differences are not large, they affect only the probabilities of particular paths, but all reactions still occur.

The termination reactions add further complexity to the composition of the pyrolysates. This complexity depends on the temperature, pressure, and time of pyrolysis. The effect of increased temperature is typically that of generating shorter molecular chains (and of changing the reaction rates). The increase in pressure affects both the pyrolysate composition and the decomposition rate. As shown for short-chain hydrocarbons, the reaction kinetic for alkane pyrolysis is typically of the first order above a certain pressure. However, as the pressure further increases at higher values (still assuming first order kinetics), an apparent increase in the reaction rate is noticed. This is in fact the result of the increase in the role of bimolecular processes (such as the hydrogen abstraction by radicals) [90]. Not only reaction rates but also the pyrolysate composition is modified in this way, more products being generated by propagation reactions. The pyrolysate composition is influenced by the degree of conversion of the initial compound. This conversion can be modified, for example, by shorter or longer pyrolysis time at a given temperature and pressure. One part of this relation is not a cause and effect process. When low conversions are caused by short decomposition time, this short time leads to the interruption of many secondary reactions, and therefore, the pyrolysate composition is modified. However, the compounds initially generated in the pyrolysate may be further decomposed, affecting the final pyrolysate composition.

An example of pyrolysis results is given in Figure 7.1.10 for hexadecane ( $\text{C}_{16}\text{H}_{34}$ ). In this case, the results were obtained at 500 °C and 0.18 atm partial pressure, and the yields are expressed as relative molar ratios for 100 moles pyrolyzed hexadecane [91]. The total conversion of parent compound was 4.9% in a dynamic system with 20.9 s residence time.

For hydrocarbons with lower molecular weight and relatively low boiling points, pyrolysis should be studied in static systems with relatively large volumes or in flow systems. In pyrolyzers typically used for solid samples, when the sample has a (relatively) low boiling point, a considerable amount of sample may vaporize before reaching the desired pyrolysis temperature, and the results do not allow a proper estimation of the amount of pyrolyzed material compared to that volatilized. Also, the application of a specific temperature for a longer time, to produce higher conversions, is not possible since the pyrolysate leaves the heating zone. However, decompositions at short pyrolysis time (such as a few seconds) can be performed in pyrolyzers used for analytical pyrolysis purposes (see Chapter 4). For example, the chromatogram of a pyrolysate (pyrogram) of *n*-pentadecane ( $\text{C}_{15}\text{H}_{32}$ ) obtained from

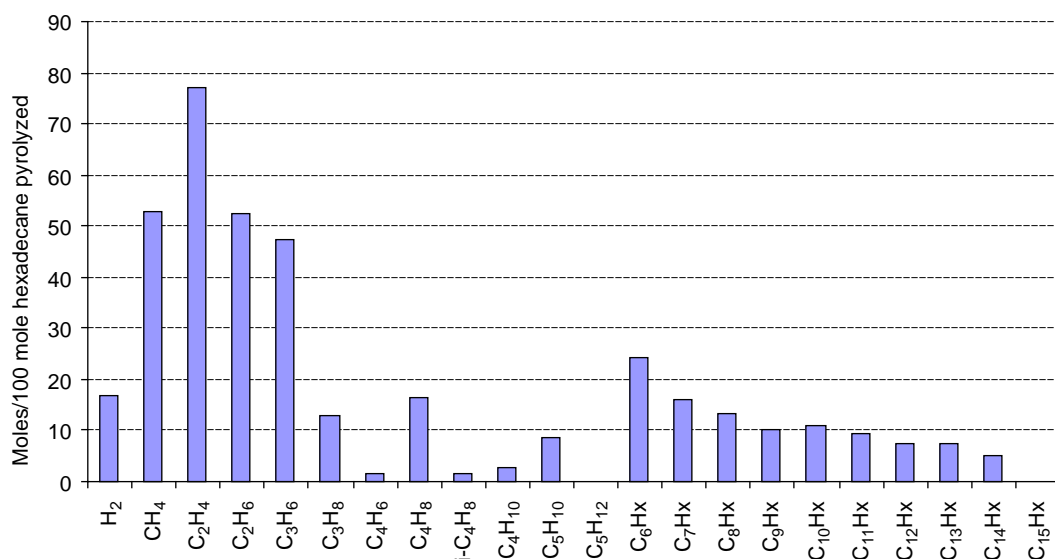


FIGURE 7.1.10. Composition of hexadecane ( $C_{16}H_{34}$ ) pyrolysate in yield of moles for 100 moles of pyrolyzed hexadecane at 500°C and 0.18 atm [91].

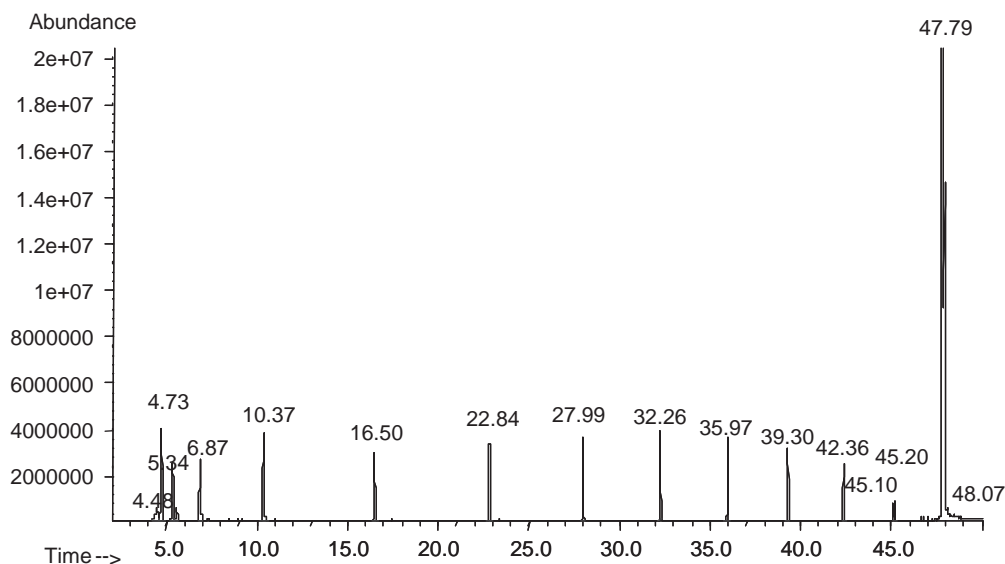


FIGURE 7.1.11. Pyrogram of *n*-pentadecane ( $C_{15}H_{32}$ ) at 900°C. Peak assignment is given in Table 7.1.6.

0.17 mg material using Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ ,  $THT = 10\text{ s}$ , and housing temperature  $T_{hou} = 280^\circ\text{C}$ , is shown in Figure 7.1.11. The pyrolysate was analyzed with conditions given in Table 4.6.1. The pyrogram obtained under identical conditions from 0.22 mg of *n*-eicosane ( $C_{20}H_{42}$ ) is given in Figure 7.1.12.

The compound identifications (performed using a GC/MS system) and their relative molar content in 100 moles of pyrolysate for each of the two compounds are given in Table 7.1.6. The calculation of the mole % was obtained based solely on peak areas, and since differences in the MS response factors can be quite large, the estimations may have large errors. *n*-Pentadecane and *n*-eicosane were excluded



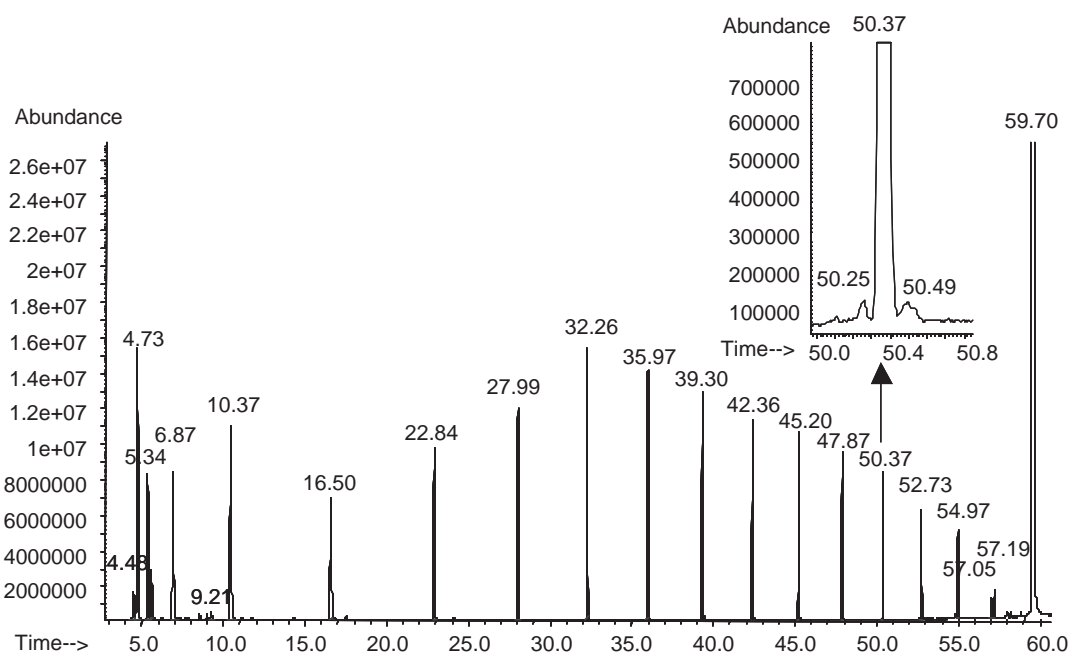
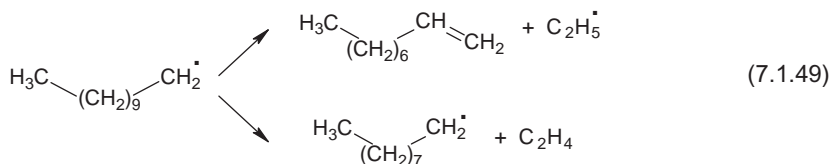


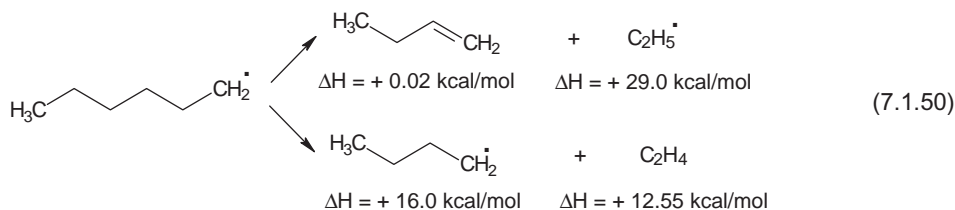
FIGURE 7.1.12. Pyrogram of *n*-eicosane ( $C_{20}H_{42}$ ) at  $900^{\circ}C$ . Peak assignment is given in Table 7.1.6. A detailed view of the time window 50.0–50.8 min is also shown. The main peak in the window is hexadecene eluting at 50.37 min with two satellite peaks, hexadecane (eluting at 50.25 min) and 1,15-hexadecadiene (eluting at 50.49 min, not visible in the main pyrogram).

from the mole % of components of their own pyrolysates, respectively. A considerable amount of sample vaporizes under the selected pyrolysis conditions.

As shown in Table 7.1.6, the main pyrolysis products of *n*-pentadecane and *n*-eicosane are the 1-alkenes with lower number of carbon atoms than the initial compound. The reactions leading to the formation of 1-alkenes are propagation and termination with disproportionation reactions.  $\beta$ -Scission plays an important role in the formation of 1-alkenes during alkanes pyrolysis. During the propagation step, a free radical with the unpaired electron on a primary carbon can undergo  $\beta$ -scission and form a 1-alkene and another free radical, as shown below in an example for the undec-1-yl radical:



Similarly, the decomposition of 1-hexyl radical is shown in the following reactions:



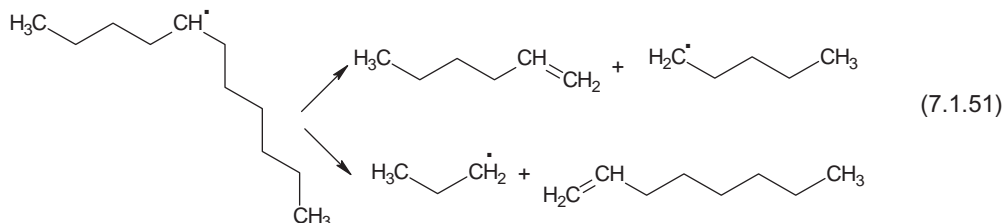
The formation of ethene is slightly favored, as seen from the enthalpies of formation of reaction products, but the difference in favor of this route is very small.

TABLE 7.1.6. Identification of peaks from the pyrograms shown in Figures 7.1.11 and 7.1.12 (*n*-pentadecane and *n*-eicosane) and their relative molar % distribution (hydrogen, methane, and ethylene were not analyzed due to the mass spectrometer settings)

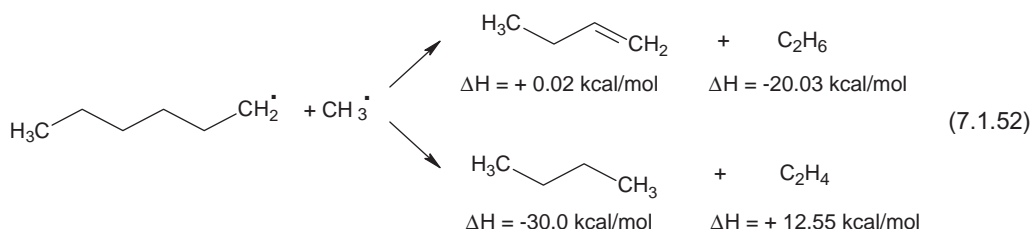
No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent <i>n</i> -pentadecane pyrolysate	Mole percent <i>n</i> -eicosane pyrolysate
1	Ethane	4.48	30	74-84-0	7.72	3.88
2	Propene	4.73	42	115-07-1	<b>25.44</b>	<b>24.36</b>
3	1-Butene	5.34	56	106-98-9	<b>11.70</b>	<b>10.38</b>
4	1,3-Butadiene	5.58	54	106-99-0	2.22	3.46
5	1-Pentene	6.87	70	109-67-1	<b>9.97</b>	<b>9.13</b>
6	2-Methyl-1-butene	7.28	70	563-46-2	0.14	Trace
7	3-Methyl-1-butene	7.55	70	536-45-1	0.11	0.12
8	1,2-Pentadiene	7.79	68	591-95-7	0.09	0.15
9	Isoprene	8.47	68	78-79-5	0.27	0.47
10	1,3-Pentadiene	8.93	68	504-60-9	0.24	0.39
11	1,3-Cyclopentadiene	9.19	66	542-92-7	0.31	0.03
12	Cyclopentene	9.21	68	142-29-0	Trace	0.64
13	1-Hexene	10.37	84	592-41-6	<b>11.88</b>	<b>11.53</b>
14	Hexane	11.01	86	110-54-3	0.16	0.14
15	3-Methylcyclopentene	14.24	98	1120-62-3	0.09	0.12
16	1-Heptene	16.50	98	592-76-7	<b>6.98</b>	<b>5.90</b>
17	Benzene	17.44	78	71-43-2	0.22	0.25
18	1-Octene	22.84	112	111-66-0	<b>5.29</b>	<b>4.56</b>
19	1,7-Octadiene	23.09	110	3710-30-3	0.03	Trace
20	1-Nonene	27.99	126	124-11-8	<b>4.43</b>	<b>4.26</b>
21	1-Decene	32.25	140	872-05-9	<b>3.95</b>	<b>4.32</b>
22	Ethenylcyclohexane	32.38	110	695-12-5	0.01	Trace
23	1-Undecene	35.97	154	821-95-4	<b>3.18</b>	<b>3.54</b>
24	1,10-Undecadiene	36.17	152	13688-67-0	0.02	Trace
25	<i>n</i> -Dodecane	39.15	170	112-40-3	0.01	Trace
26	1-Dodecene	39.30	168	112-41-4	<b>2.45</b>	<b>2.84</b>
27	1,11-Dodecadiene	39.39	166	5876-87-9	Trace	Trace
28	1-Tridecene	42.36	182	2437-56-1	<b>1.78</b>	<b>2.35</b>
29	1,13-Tridecadiene	42.47	180	21964-49-8	0.01	Trace
30	Tetradecane	45.10	198	629-59-4	<b>0.47</b>	Trace
31	1-Tetradecene	45.20	196	1120-36-1	<b>0.57</b>	<b>2.00</b>
32	1,13-Tetradecadiene	45.20	194	21964-49-8	Trace	Trace
33	Pentadecane	47.79	212	629-62-9	Not included	Trace
34	1-Pentadecene	47.87	210	13360-61-7	<b>0.28</b>	<b>1.66</b>
35	1-Hexadecene	50.37	224	1120-36-1	—	<b>1.39</b>
36	1-Heptadecene	52.73	238	6765-39-5	—	<b>0.99</b>
37	Octadecane	54.84	254	593-45-3	—	Trace
38	1-Octadecene	54.97	252	112-88-9	—	<b>0.73</b>
39	Nonadecane	57.05	268	629-92-5	—	0.18
40	1-Nonadecene	57.19	266	18435-45-5	—	<b>0.24</b>
41	Eicosane	59.57	282	112-95-8	—	Not included
42	1-Eicosene	59.60	280	3452-07-1	—	Trace

Note: 1-alkene moles % values are written with bold characters.

1-Alkenes also are formed from radicals with the unpaired electron on a secondary atom, as shown below for undec-5-yl radical undergoing a  $\beta$ -scission:



The formation of 1-alkenes by termination reactions with disproportionation would predict the formation of both alkanes and 1-alkenes, as shown below for the case of the reaction of hexyl and methyl radicals.



There is no considerable thermodynamic advantage for the formation of a specific alkene or alkane in the terminations with disproportionation of the type shown in rel. 7.1.52, and therefore, the occurrence of each of the two routes should have about equal chance. As seen in Table 7.1.6, higher levels of shorter alkanes are found in the pyrolysate (ethene not shown) of both *n*-pentadecane and *n*-eicosane, but the 1-alkenes are always at much higher levels. This would indicate that the termination with disproportionation reactions of the type shown in rel. 7.1.52 do not play a very important role in this pyrolysis. For larger fragment molecules the ratio alkene/alkane tends to increase, indicating that the larger fragments are indeed formed with higher participation of termination reactions.

Some 1,*n*-alkadienes with lower number of carbons also are generated by pyrolysis. These are formed by reactions similar to those of 1-alkenes by scissions of compounds already having a double bond at the other end of the molecule. The alkenes formed in the pyrolysis reaction (see reaction 7.1.51) may pyrolyze further, as discussed later in Section 7.3. Their thermal decomposition may lead to the formation of either shorter alkenes or of 1,*n*-alkadienes.

A few branched hydrocarbons, as well as benzene, cyclopentadiene, and 3-methylcyclopentadiene, were detected in *n*-pentadecane and *n*-eicosane pyrolysates. These compounds are true pyrolysis products, but the interpretation of the results of pyrolysis should be done with special attention. Some compounds may originate from impurities in the initial material subjected to pyrolysis. The purity of the initial compound was verified by an identical chromatographic separation as that used for the pyrolysate, applied on a sample of *n*-pentadecane or *n*-eicosane dissolved in cyclohexane, with typical liquid injection in a GC/MS system. Also, it must be emphasized that important pyrolysate constituents such as hydrogen, methane, and ethylene were not seen in the pyrogram, although these compounds are present in the pyrolysate. In the described experiment of *n*-pentadecane and *n*-eicosane Py-GC/MS, the mass range for the mass spectrometer used as detector was set above  $m/z = 28$  in order to avoid the interference of traces of  $\text{N}_2$  from air, but analytes such as  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_4$  have  $\text{MW} \leq 28$ .

As the molecular weight and boiling point of the sample to be pyrolyzed increase, use of standard pyrolysis instrumentation becomes a more common technique for pyrolysis studies of solid samples. The results of pyrolysis of *n*-trtriacontane ( $\text{C}_{33}\text{H}_{68}$ ) obtained from 0.13 mg material using Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing

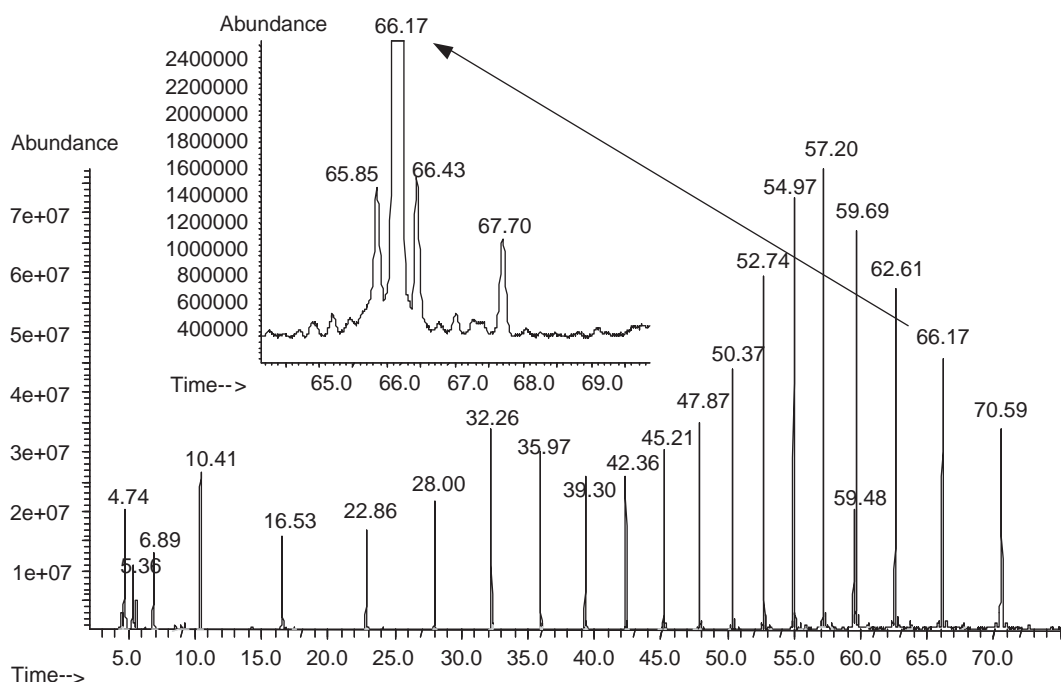


FIGURE 7.1.13. Pyrogram of *n*-tritriacontane ( $C_{33}H_{68}$ ) at  $900^{\circ}C$  for 10 s. A detailed view of the time window 64.0–70.0 min is also shown. The main peak in the window is docosene eluting at 66.17 min with two satellite peaks, docosane (eluting at 65.85 min) and 1,21-docosadiene (eluting at 66.43 min).

temperature  $T_{\text{hou}} = 280^{\circ}C$ , are shown in Figure 7.1.13. The analysis of pyrolysate was done with conditions in Table 4.6.1.

For the chromatogram of *n*-tritriacontane pyrolysate, peak identification for the compounds up to eicosene (Ret. time 59.69 min in Figure 7.1.13) is identical to that shown in Table 7.1.6. The large peaks in the figure with longer retention times are 1-heneicosene ( $C_{21}H_{42}$  at 62.61 min), 1-docosene ( $C_{22}H_{44}$  at 66.17 min), and 1-tricosene ( $C_{23}H_{46}$  at 70.59 min). The pyrolysate also contains all the 1-alkenes ( $C_nH_{2n}$ ) with  $n$  up to 33, but the compounds with  $24 \leq n \leq 33$  are not shown in the pyrogram from Figure 7.1.13. Due to the high boiling points of these compounds, they did not elute from the chromatographic column (DB-1701) in the selected experimental conditions. A different chromatographic column (e.g., a thin film methyl silicone column) and higher GC oven temperatures are necessary for the analysis of these compounds ( $C_{24}$  to  $C_{33}$ ). The complete analysis of the pyrolysates should always take into consideration the limitations of the analytical instrument used for pyrolysate separation and measurement. The pyrogram may show all or only some of the pyrolysate components. Particular attention should be given to the conditions for the analysis of nonvolatile, very polar, or very low-molecular-weight compounds, which may not be included in the range of instrument detection.

A detailed view of a narrow range in the chromatogram from Figure 7.1.13 (window of 64–70 min) shows the major peak of the 1-alkene ( $C_{22}H_{44}$ , 1-docosene in this case) and that of two small satellite peaks, one being the corresponding alkane ( $C_{22}H_{46}$ , docosane), the other being the corresponding 1,*n*-alkadiene ( $C_{22}H_{42}$ , 1,21-docosadiene). A small peak at 67.7 min was tentatively identified as 1-eicosanal ( $C_{20}H_{40}O$ ). Similar peaks are seen associated with other alkenes in the pyrolysate. The formation of an oxygenated compound from a saturated hydrocarbon may be caused by the presence of oxygen traces during pyrolysis.

Pyrolysis of branched hydrocarbons follows a pattern very similar to that of normal hydrocarbons [71]. The formation of various isomers and the difficulty of the correct assignment of a specific isomeric structure based on mass spectral analysis adds difficulty to isomer identification. As general observations, the composition of pyrolysates of branched compounds also depends on temperature,

pressure, and extent of conversion. The increase in temperature above 650 °C has the typical effect of increasing the proportion of lighter pyrolysis components, especially of methane, ethylene, and hydrogen. Branched hydrocarbons with secondary and tertiary carbons decompose more easily than normal hydrocarbons in general. Quaternary carbons are typically more stable than others.

Since alkane pyrolysis is related to industrial pyrolysis of oil fractions (containing large proportion of alkanes) and the oil fractions are mixtures of various hydrocarbons, pyrolysis of unique compounds serves only for reaction models. Of higher practical value is the information on pyrolysis of hydrocarbon mixtures [92]. As seen on single hydrocarbons, the pyrolysis process of hydrocarbons takes place mainly through free radical mechanisms. Therefore, it is expected that the free radicals formed from one component of the mixture will affect the molecules of another component. However, since the free radicals generated from hydrocarbons are basically the same, the result of pyrolysis is not significantly different for mixtures than for individual components. Only some changes in the rate of pyrolysis can be observed, mainly when the decomposition of different components takes place at significantly different rates. In this case, the effect is a decrease in the rate of decomposition of the fast reacting compound and an increase in the rate of decomposition of the slow reacting compound.

Pyrolysis in the presence of other compounds, including olefins, aromatics, steam (H<sub>2</sub>O), and hydrogen, also were studied for individual or mixtures of alkanes [40,65,76,77,93]. Generally, olefins inhibit the thermal decomposition of alkanes, while olefins decompose at a higher rate in the presence of alkanes. Since olefins are generated during alkanes pyrolysis, in practical applications on petroleum (which usually does not contain olefins initially), the inhibition effect of olefins is seen as a self-inhibition process.

Pyrolysis in the presence of hydrogen shows an increase in light hydrocarbons including methane, ethylene, ethane, and a decrease in the formation of higher olefins and of carbon (coke and soot) [92].

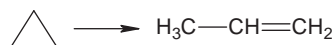
## 7.2. CYCLIC SATURATED HYDROCARBONS

### *General aspects*

Cyclic saturated hydrocarbons (cycloalkanes) are hydrocarbons containing one or more saturated rings of carbon atoms in their molecule. The rings may have three or more carbon atoms. Several cycloalkanes, mainly the homologs of cyclopentane and cyclohexane, are present in large amounts in nature in crude oil. This class of compounds is also known as naphthenic hydrocarbons. Naphtha is a fraction of refined petroleum that contains large proportions of these compounds. Among the cycloalkanes are compounds with two or more fused cycles, such as decalin (decahydronaphthalene), norbornane (bicyclo[2.2.1]heptane), adamantane (tricyclo[3.3.1.1<sup>3,7</sup>]decane), and [1,1,1]propellane. Special classes of cyclic saturated hydrocarbons include platonic hydrocarbons (cubane C<sub>8</sub>H<sub>8</sub>, dodecahedrane C<sub>20</sub>H<sub>20</sub>), macrocycle hydrocarbons, etc.

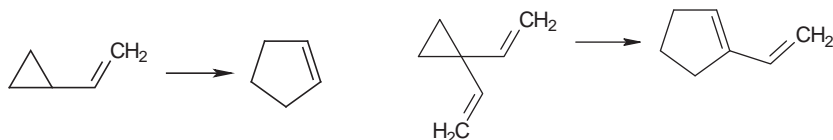
### *Cyclopropane and cyclobutane*

Cycloalkanes with the lowest number of carbons are cyclopropane (C<sub>3</sub>H<sub>6</sub>) and cyclobutane (C<sub>4</sub>H<sub>8</sub>). Both cyclopropane and cyclobutane have bond angles between the carbon atoms that deviate considerably from that of normal sp<sup>3</sup> carbon bonds, which is 109.5°. For this reason, these molecules exhibit relatively high ring strain energy. It is estimated that the energy of ring strain for cyclopropane is 27.6 kcal/mol and that of cyclobutane is 26.4 kcal/mol. These compounds decompose relatively easily upon heating (see Section 2.4). The common decomposition reaction of cyclopropane is shown below:



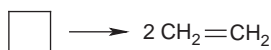
When cyclopropane ring has substituents (or is a substituent to another molecular moiety), the resulting pyrolysis product can be different, as shown in reaction 2.4.2. Two additional examples of

pyrolysis outcome for compounds containing a cyclopropane ring are shown below:



The reactions occur by a 1,3-sigmatropic shift.

The mechanism of cyclobutane pyrolysis shows some peculiarities and generates ethylene, as follows:



This reaction seems to occur by a concerted mechanism, and no free radicals were detected using very low pressure pyrolysis with the trapping of the pyrolysis products in a low temperature matrix (LTM) of solid nitrogen followed by infrared (IR) spectroscopy (LTM/IR) [94]. The expected isomerization reaction of cyclobutane into 1-butylene does not seem to take place during cyclobutane pyrolysis at low pressure.

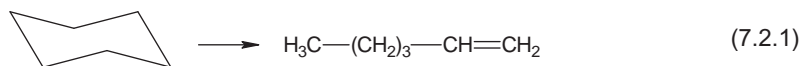
### Cyclopentane, cyclohexane, and their alkyl substituted homologs

Pyrolysis of cyclohexane and of substituted cyclohexanes, as well as of cyclopentanes, has considerable industrial importance related to the formation of useful compounds such as ethylene. For industrial purposes, pyrolysis is typically performed on mixtures (e.g., naphtha fraction), but studies on individual compounds have their own importance for the understanding of the pyrolysis of hydrocarbon mixtures [95,96].

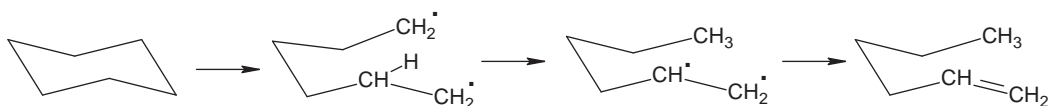
The ring strain of cyclopentane is about 6.5 kcal/mol, and that of cyclohexane is zero. The ring strain does not play an important role in the pyrolysis of these compounds. Unsubstituted cycloalkanes can be slightly more stable during pyrolysis compared to the corresponding alkanes, while the reverse is true for the substituted ones.

Pyrolysis of cyclohexane in the temperature interval 750–900 °C generates 1-butene as a main component, and also 2-butene, butadiene, and ethylene. The studies were performed for the compound in gas phase, since flash pyrolysis as applied to solid samples is not an appropriate technique for the study of compounds with low boiling points.

The first initiation step in cyclohexane pyrolysis is very likely the formation of a biradical as the result of a C–C bond cleavage. The studies on cyclohexane pyrolysis at low pressure with the trapping of the pyrolysis products in a LTM [94] show that the main result is the isomerization of cyclohexane to the corresponding 1-hexene:

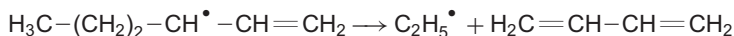
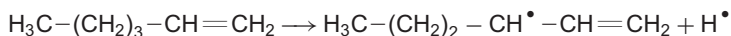


This reaction seems to take place as a result of the following steps (after the formation of the biradical in the initiation step):

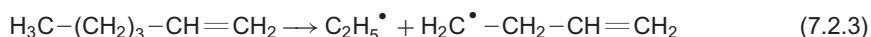
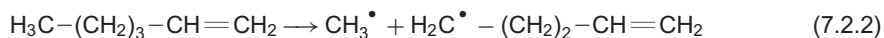


As a result of further pyrolysis of 1-hexene, cleavages of both C–C and C–H bonds may occur. From a C–H cleavage, several main pyrolysis products can be formed as shown in the reaction below for the

formation of butadiene:

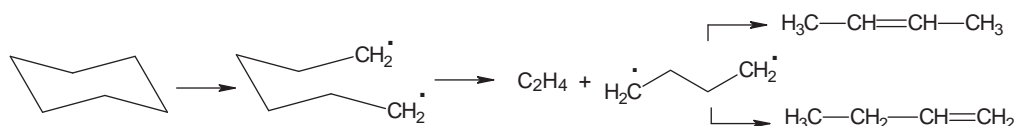


The radical generated from pyrolysis of 1-hexene by the elimination of an  $\text{H}^\bullet$  atom is relatively stable, having the unpaired electron in the allyl position. However, the formation of a hydrogen atom is a strongly endothermic process (see Table 3.1.4), and the hexene pyrolysis proceeds mainly with a C–C cleavage as shown in reactions below:

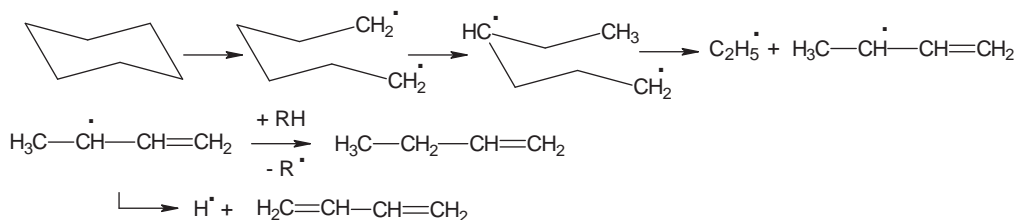


The free radicals formed in these reactions will continue the reaction propagation process with the formation of butenes, butadiene, and traces of methane, propene, pentene, etc.

At higher temperatures, butenes and ethylene can be generated directly from cyclohexane biradical following a  $\beta$ -cleavage (to the atom with the unpaired electron) of a C–C bond as shown below:



Cyclohexane biradical also can undergo an isomerization and  $\beta$ -cleavage with the formation of 1-butene and butadiene:

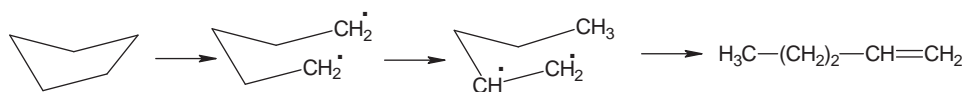


Other reactions may occur during cyclohexane pyrolysis. Some may take place with formation of smaller molecules caused by further pyrolysis of butenes, and others take place with the formation of heavier compounds as a result of various condensation reactions. Formation of carbon as the end result of cyclohexane pyrolysis can be traced through precursors such as 1-hexene [97], 1,3-butadiene [98,99], benzene [100], and compounds with condensed aromatic rings [101]. Most studies show that the formation of the aromatic rings in the case of cycloalkanes does not take place directly from the cycle. A cycle opening followed by the formation of unsaturated compounds and eventually of the aromatic compounds is the most likely path for aromatic ring formation. The proof of this mechanism was obtained by studying the pyrolysis of cycloalkanes with exocyclic  $^{14}\text{C}$ -labeled carbons [102]. The exocyclic-labeled  $\alpha$ -carbon was found included mainly in the aromatic rings formed by pyrolysis and not in the side substituents.

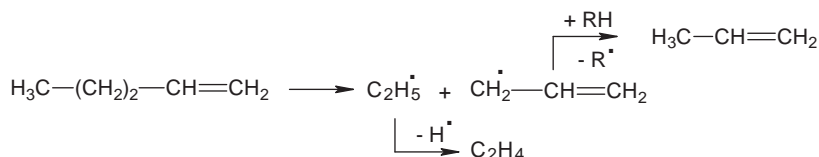
At higher temperatures, the cleavage of a C–H bond from cyclohexane with the formation of a cyclohexyl radical becomes another potential reaction path during pyrolysis, although the cleavage of a bond of the type  $\text{RH}_2\text{C}-\text{CH}_2\text{R}$  requires about 80.5 kcal/mol, while the cleavage of a bond of the type  $\text{R}_2\text{HC}-\text{H}$  requires 94.2 kcal/mol. Cyclohexyl radical can further generate 1-hexene, butenes, or butadiene. Detailed kinetic parameters for hexane pyrolysis are available in the literature [94,103–105].

Oxidative pyrolysis of cyclohexane may occur by stepwise dehydrogenation leading to benzene formation. This was demonstrated in a study of a stoichiometric flat flame of cyclohexane/O<sub>2</sub> in 32.5% Ar at 20 Torr pressure and 35.0 cm/s feed velocity [106].

Cyclopentane pyrolysis in gas phase includes basically the same type of reactions as for cyclohexane. There is evidence that the first step in the reaction is the formation of a biradical that undergoes isomerization to 1-pentene:



This reaction is followed by the decomposition of 1-pentene with formation of ethene and propene as shown below:



This formation of propene and ethylene can be viewed as a retro-ene reaction. In the pyrolysis of cyclopentane, there were identified traces of cyclopropane [107], possibly generated directly from cyclopentane biradical:

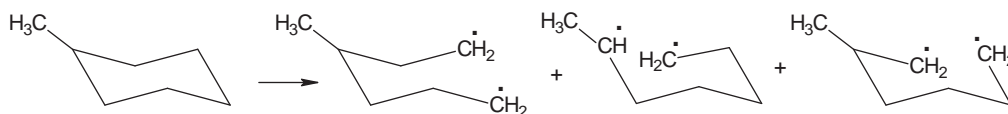


At higher temperatures, a C-H bond from cyclopentene can cleave, with the formation of a cyclopentyl radical. This radical may generate cyclopentene in a reaction as shown below [94]:

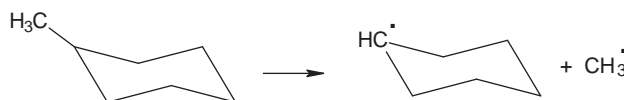


Other reactions with the formation of different radicals including CH<sub>3</sub><sup>•</sup>, C<sub>2</sub>H<sub>5</sub><sup>•</sup>, and C<sub>3</sub>H<sub>7</sub><sup>•</sup> take place during cyclopentane pyrolysis [108].

Pyrolysis of alkylcyclohexane and alkylcyclopentane shows considerable similarities with the pyrolysis of non-substituted cyclohexane and cyclopentane [71,109]. However, the process has additional complexity. For example, pyrolysis of methylcyclohexane begins with the cleavage of a C-C bond from the cycle, but different biradicals can be generated, as shown below:



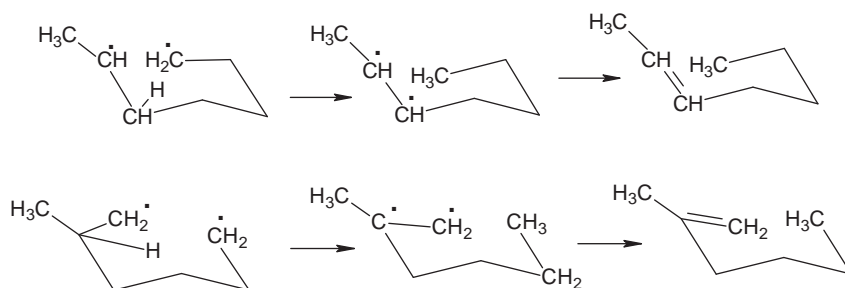
The cleavage of the C-C bond of the methyl group also can occur:



As previously indicated, the cleavage of the bond RH<sub>2</sub>C-CH<sub>2</sub>R requires about 80.5 kcal/mol, that of the bond R<sub>2</sub>HC-CH<sub>2</sub>R requires about 78.2 kcal/mol, and that of a bond R<sub>2</sub>HC-CH<sub>3</sub> requires about



83.2 kcal/mol (see Table 3.1.2). This suggests that the probability of each of these reactions is not very different from each other, although, compared to the cleavage of the bond between two secondary carbons, the cleavage between a tertiary carbon and a secondary carbon is slightly more favorable, and that between a tertiary carbon and a methyl is slightly less favorable. Each of the radicals formed in previous reactions can continue the reaction (propagation step) with rearrangements similar to reaction 7.2.1, as shown in the following two examples:



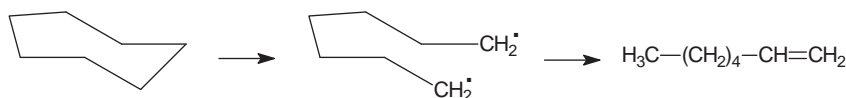
The complexity of propagations and terminations will lead to a considerable number of reaction products including linear and branched heptenes, linear and branched pentenes, isoprene, propene, ethene, and methane. Cyclohexene and cyclohexadiene also were detected in pyrolysis products. At temperatures above 670 °C, aromatic hydrocarbons including benzene and toluene start forming, but they are only at trace levels. At temperatures between 700 °C and 750 °C, the yields of benzene and toluene are around 13 and 5%, respectively. The study of methylcyclohexane with  $^{14}\text{C}$ -labeled methyl group demonstrated that about 33% of benzene and 45% of toluene contained labeled carbon atoms in the aromatic ring [102]. This indicated the opening of the cycloalkane cycle during pyrolysis, before the formation of aromatic compounds that are a result of further condensation reactions.

Similar to the case of alkanes, the burning of cycloalkanes is an important subject related to fuel characterization [110] and behavior in internal combustion engines. Several studies on the correlation between the octane number (RON) and the cycloalkane structure were performed [111,112], since many cycloalkanes are present in common fuels (e.g., gasoline). Cycloalkanes combustion starts with an early pyrolytic process resulting in the formation of free radicals, similar to that seen for alkanes [113]. Once the free radicals are formed, the interaction with the oxygen molecules continues the combustion process, which is strongly exothermic. Formation of hydroperoxides and peroxides also is involved in cycloalkane combustion in a similar manner as for alkanes. The kinetic parameters of hundreds of reactions involved in burning of cycloalkanes are reported in the literature [111].

### Cycloalkanes with higher number of carbons in the cycle

Cycloalkanes with a higher number of carbons in the cycle, including cycloheptane and cyclooctane, pyrolyze basically by the same mechanisms as cyclopentane or cyclohexane. The ring strain energy of these compounds does not play a major role in pyrolysis, although up to  $\text{C}_9\text{H}_{18}$  the ring strain energy increases as shown in Figure 7.2.1. The cycle in cycloalkanes larger than  $\text{C}_9\text{H}_{18}$  starts folding in advantageous conformations and the ring strain energy decreases. The pyrolysis of larger cycloalkanes typically starts with the cleavage of a C—C bond and the formation of a biradical.

This biradical will continue a propagation process. One likely path for the biradical further reaction is the formation of a 1-alkene that continues the pyrolysis process with the generation of various fragments. This possibility is exemplified below for cycloheptane:



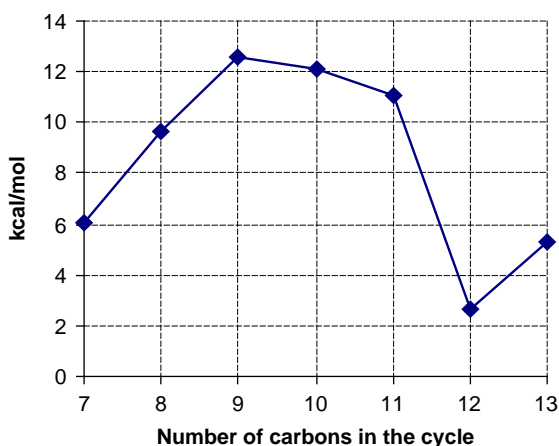
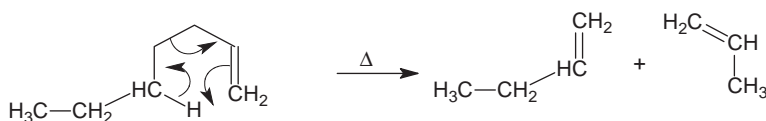


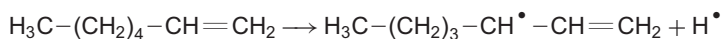
FIGURE 7.2.1. Variation of ring strain energy with the number of carbons in cycloalkanes.

1-Heptene by pyrolysis generates mainly butene and propene in a retro-ene reaction as shown below:

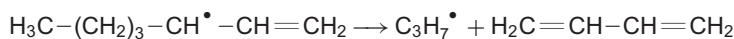


The mechanism of this reaction does not necessarily involve free radicals. The proof of the formation of 1-heptene from cycloheptane as a first stage of decomposition was obtained by showing the close similarity between the composition of their pyrolysates using the trapping of the products in a LTM of nitrogen followed by an IR study (LTM/IR evaluation) [94].

Another potential first stage in the pyrolysis reaction of 1-heptene is the formation of a hydrogen atom and a radical with the unpaired electron in allyl position, similar to the radicals found in the case of 1-hexene:

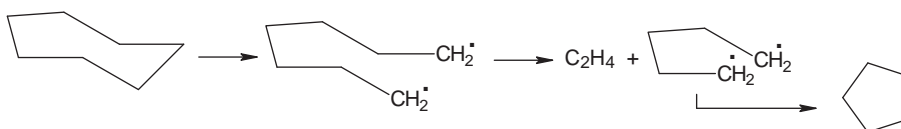


The radical may generate butadiene and propene by a  $\beta$ -scission to the atom bearing the free radical:



In a similar reaction cyclooctane generates pentene and propene, and also butadiene and butyl radicals. This radical is a source of 1-butene that is present in cyclooctane pyrolysate.

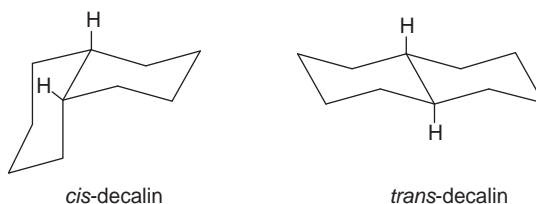
Another path for further reaction of cycloheptane biradical is a rearrangement with the formation of a smaller, more stable cycle of cyclopentane, as shown below:



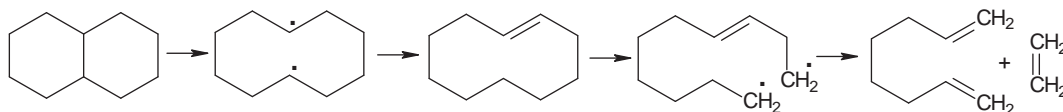
Further heating of cycloalkanes leads to the formation of aromatic hydrocarbons including benzene, naphthalene, and traces of PAHs. The formation of carbon is the final phase of pyrolysis.

### Decalin

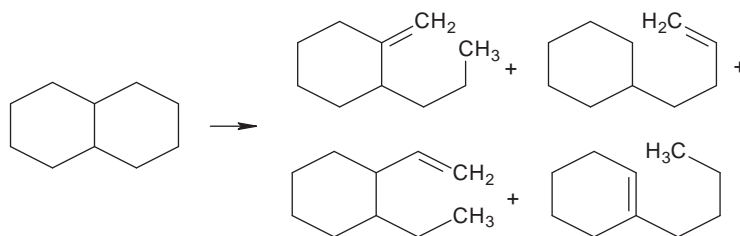
Decalin is a bicyclic saturated hydrocarbon (bicyclo[4.4.0]decane) usually obtained from naphthalene catalytic hydrogenation. Decalin is used mostly as a solvent. Its pyrolysis presents interest since decalin has been used as a model compound for the jet propellant JP-8 fuel. Pyrolysis of decalin in gas phase has been studied by various techniques [114–117], and the results received different interpretations regarding reaction mechanisms. Decalin can be present in two conformations indicated as *cis*-decalin and *trans*-decalin. Their formulas are shown below:



Pyrolysis results do not differ between the two forms since the difference in the heat of formation of the compounds is only about 3.1 kcal/mol (in gas form –40.4 kcal/mol for *cis*-decalin and –43.5 kcal/mol for *trans*-decalin, which is slightly more stable). Pyrolysis at temperatures around 1000 °C generates numerous fragment molecules including propene, 1,4-pentadiene, 1,6-heptadiene, butadiene, cyclopentadiene, ethylene, ethenylcyclohexane, and bicyclo[4.4.0]decenes. Several studies indicated as a first step in pyrolysis the following sequence of reactions [118,119]:

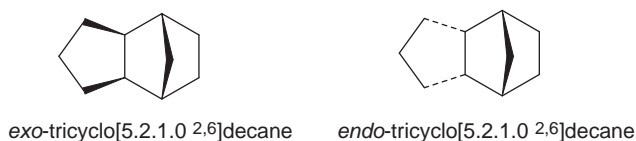


Further rapid decomposition of 1,7-octadiene may be responsible for the generation of smaller fragments. Other mechanisms involve as the first step the formation of cycloalkanes with alkenyl substituents as indicated below:



The decomposition of the substituted cycloalkanes may be the source of decalin pyrolysis products [117]. The presence of traces of bicyclo[4.4.0]decenes in the pyrolysate indicates that a 1,4-H<sub>2</sub> elimination is possible, followed by a 1,3-H migration.

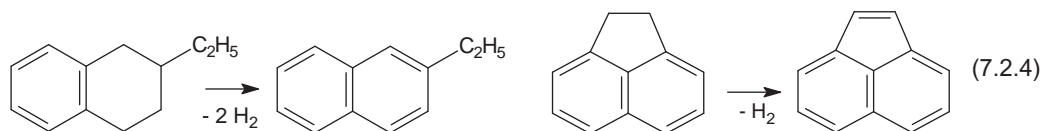
Among the hydrocarbons with more than two cycles for which the thermal decomposition has been studied is tricyclo[5.2.1.0<sup>2,6</sup>]decane (tetrahydrodicyclopentadiene). This compound can be found in *exo* and *endo* forms, the *exo* form being used in the polymer industry and as the main component of JP-10 high-energy-density fuel.



The fuel has 96–97% *exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane and, in addition, some *endo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane, decahydronaphthalene, and adamantane. Because of its importance as a fuel, the pyrolysis of the *exo* form has been intensely studied [120–124]. When the JP-10 fuel is heated for 90 min at 425 °C, the analysis shows the formation of *n*-propane, *n*-butane, cyclopentane (main decomposition product), methylcyclopentane, 1-methylcyclopentene, benzene, ethylcyclopentane, ethylidencyclopentane, toluene, *n*-propylcyclopentane, *cis*-biyclo[3.3.0]oct-2-ene, ethylbenzene, *o*-xylene, octahydropentylene, and 3-methylcyclooctane. Thermal decomposition of *exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane in the range 848–933 K generates hydrogen, methane, ethylene, ethane, propene, 1,3-cyclopentadiene, benzene, 1,5-hexadiene, toluene, 3-cyclopentyl-cyclopentene, and traces of cyclopentene. At higher temperatures, acetylene, propyne, and other small molecules are generated [120]. The initiation steps of pyrolysis involve biradical formation, similar to the case of decalin [125].

### Other cycloalkanes

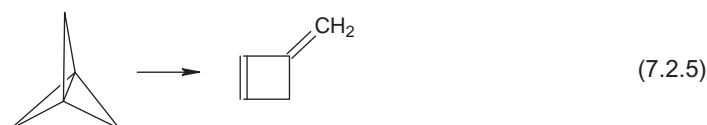
The reactions discussed in this section are typical for the decomposition under the influence of heat of a saturated cycle. Numerous other reactions may be influenced by the particular structure of the parent molecule. Particularly, the process is affected by the tendency of formation of more stable molecules. For example, the presence of an aromatic ring in the molecular structure may influence the outcome of the pyrolytic process. This is shown below for two examples: pyrolysis of 2-ethyltetrahydro-naphthalene (2-ethyltetralin) and pyrolysis of acenaphthene.



The formation of stable compounds with higher aromaticity or with higher conjugation influences the result of the reactions 7.2.4.

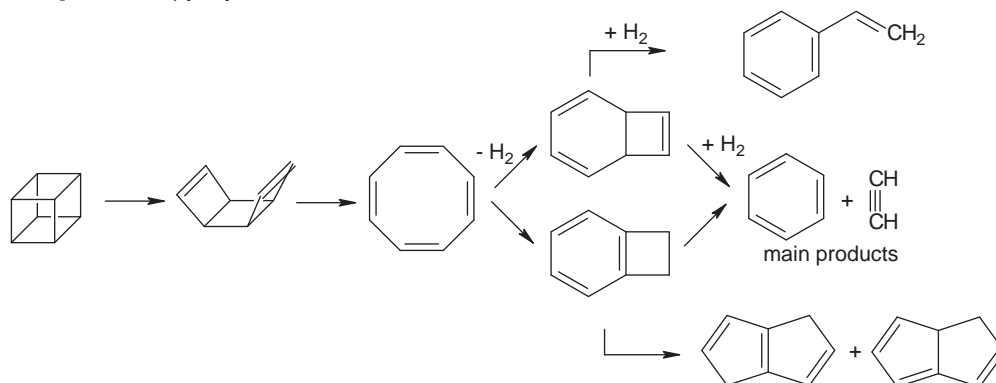
### Compounds with highly strained cycles

Pyrolysis of the compounds with highly strained cycles presents interest in relation to their combustion since these compounds have the potential for generating a large amount of energy (for a given volume of material) upon burning. One such compound with highly strained rings is [1.1.1]propellane, which has a strain energy of 102 kcal/mol. This compound decomposes at low temperatures and is not a candidate for a high-energy fuel. At 114 °C the half-life of this compound is 5 min, generating 3-methylenecyclobutene as shown in the reaction below:



Other compounds, such as cubane or methylcubane are more stable, and while cubane is solid and not very soluble in other hydrocarbons, methylcubane is a liquid, which makes this compound considered to be a potential high-energy fuel. The strain energy for cubane is about 160 kcal/mol. This compound decomposes at 230–260 °C, mainly with the formation of benzene and acetylene. At elevated pressure, the pyrolysate has a higher content of cyclooctatetraene, which is considered an intermediate compound in the formation of benzene and acetylene. Lower levels of styrene, 1,4-dihydropentalene, and 1,5-dihydropentalene also were detected in pyrolysis products of cubane

[126,127]. Cubane pyrolysis is shown in the reactions below:



A thermal decomposition mechanism similar to that of cubane was found to explain the decomposition of methylcubane [126].

### 7.3. ALKENES

#### General aspects

The compounds discussed in this section are hydrocarbons containing one double bond ( $C=C$ ) in their molecule and are known as alkenes or olefins. The presence in nature of alkenes is less common than that of saturated or aromatic hydrocarbons, since they are reactive compounds. However, large amounts of alkenes are produced in the oil industry by thermal processing of other hydrocarbons and in coal processing to produce coke. Alkenes are very important industrial products used for the preparation of plastics and rubbers (polyethylene, polypropylene, polyisobutylene, etc.) and of industrial solvents (some by chlorination). The main sources of alkenes involve pyrolytic processes of other hydrocarbons. During this process, not only are alkenes generated, but also their own pyrolysis may take place diminishing the production yield. For these reasons, the pyrolysis of this class of compounds has been thoroughly studied [128–131]. The formation of soot in industrial pyrolysis of olefins [132] and of PAHs are of particular interest (see Section 7.8).

The electronic model for the double bond of alkenes assumes that each of the two carbons involved in the bond have three  $sp^2$  hybrid orbitals and one  $p_z$  atomic orbital. The  $sp^2$  orbitals form  $\sigma$  bonds and the  $p_z$  orbitals form  $\pi$  bonds. The double bond consists of a  $\sigma$  bond and a  $\pi$  bond between two carbon atoms. The average dissociation energy of a  $C=C$  bond is 146–151 kcal/mol ( $173.3 \pm 1.2$  kcal/mol for  $CH_2=CH_2$  as reported in [133]), the variation in this value depending on the other substituents to the carbon atoms involved in the double bond. The thermal stability of a double bond is much higher than that of a single  $C-C$  or  $C-H$  bond (65–83 kcal/mol for a  $C-C$  bond and 96–99 kcal/mol for a  $C-H$  bond). Since the hydrocarbons containing a double bond also contain  $\sigma$  bonds of the type  $C-C$  and  $C-H$ , the molecules under the influence of heat are likely to undergo a cleavage of one (or more) of these  $\sigma$  bonds before the double bond cleaves. The position of the single bonds that cleave in a molecule containing a double bond is influenced by the position of the double bond. Many thermal decompositions of olefins have a free radical mechanism similar to that encountered for alkanes. However, other reactions besides bond cleavage are common for alkene pyrolysis. Formation of dienes and further condensation reactions (Diels–Adler type or with radicalic mechanism) explain the formation of aromatic hydrocarbons in olefin pyrolysis. Also, retro-ene reactions (see Section 2.3) account for some of the components of alkene pyrolysates.

#### Ethylene

Ethylene (ethene)  $C_2H_4$  is the simplest hydrocarbon with a double bond. The compound is obtained industrially in large quantities as an intermediary compound for the synthesis of many consumer products.

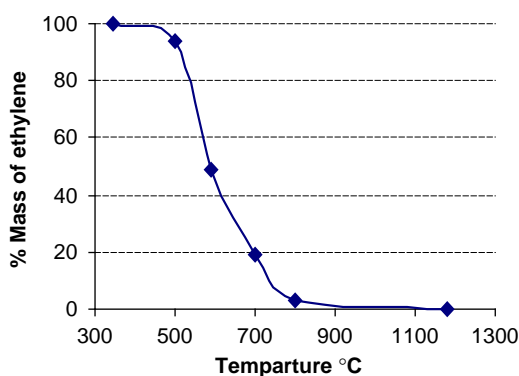


FIGURE 7.3.1. Percentage mass of ethylene remaining at different temperatures when the compound is heated for 30 min.

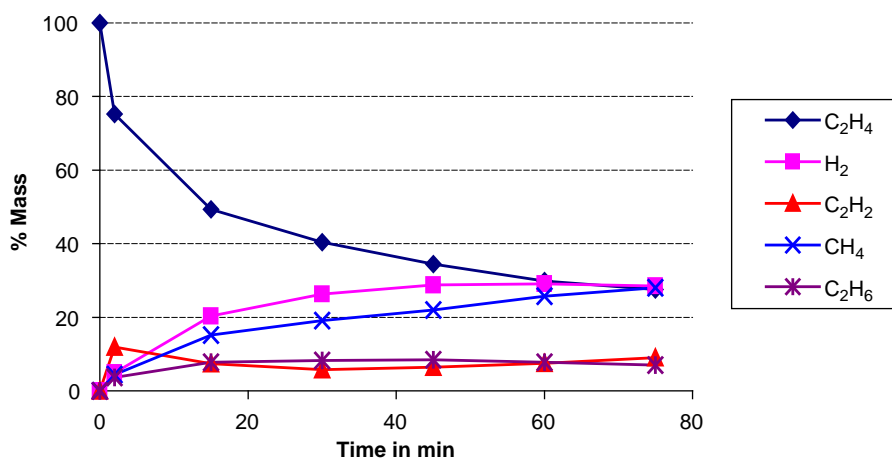
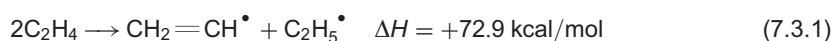


FIGURE 7.3.2. Composition of ethylene pyrolysate as a function of heating time, at 570–580 °C and 350 Torr pressure under continuous heating.

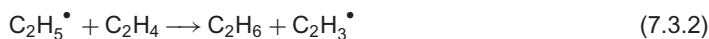
Since ethylene is obtained almost entirely by pyrolysis (from naphtha, ethane, propane, etc.), its own pyrolysis (typically undesired) is the subject of numerous studies [96,134]. Pyrolysis of ethylene was mentioned previously in connection with methane and ethane pyrolysis (see Section 7.1). The products of ethylene pyrolysis depend considerably on temperature, pressure (or partial pressure when the pyrolysis takes place in the presence of an inert diluent), and time of exposure to the elevated temperature [128].

Pyrolysis of ethylene starts to be noticed around 500 °C. With the increase in temperature, less and less ethylene remains intact, generating hydrogen, methane, acetylene, ethane, etc. The variation of the mass of ethylene after 30 min of heating at different temperatures is shown in Figure 7.3.1. The decomposition was found to follow a reaction order between first and second, with a constant of the form  $k = 10^{11.73} \exp[-49617(\text{cal/mol})/RT] \text{ cm}^{3/2}/\text{mol}^{1/2}/\text{s}$  [135]. The composition of ethylene pyrolysate as a function of heating time at 570–580 °C and 350 Torr pressure under continuous heating is shown in Figure 7.3.2.

A detailed analysis of ethylene pyrolysis at very small conversions (at the beginning of the pyrolytic process) and partial pressures varying between 25 Torr and 600 Torr showed that at temperatures below 900–1000 K the initiation of the pyrolysis process is dominated by the formation of vinyl and ethyl radicals as shown below:



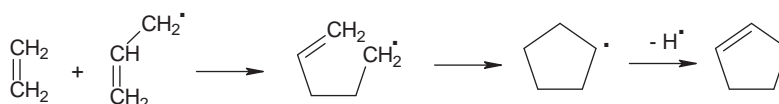
The enthalpy of formation of the vinyl radical is higher than that of ethyl radical (see Table 3.1.4), making the decomposition of ethene more endothermic than that of ethane. Ethylene is the most thermally stable olefin. The main products generated following the initial free radicals formation, at these temperatures and at low conversion, are  $C_2H_6$ ,  $C_3H_6$ ,  $1-C_4H_8$ , and  $1,3-C_4H_6$ , with lower amounts of  $C_2H_2$ ,  $CH_4$ , and  $H_2$ . The  $C_2H_2$  and  $1,3-C_4H_6$  result from reactions of  $C_2H_3^\bullet$ , while  $C_2H_6$ ,  $C_3H_6$ , and  $1-C_4H_8$  result from reactions of  $C_2H_5^\bullet$ . The formation of  $C_2H_2$  takes place almost exclusively from the decomposition of the  $C_2H_3^\bullet$  radical. The free radicals formed in this reaction become involved in propagations of the type:



Further decompositions generate a mixture of radicals including, besides  $C_2H_3^\bullet$  and  $C_2H_5^\bullet$ , radicals such as  $H^\bullet$ ,  $CH_3^\bullet$ ,  $C_3H_7^\bullet$ ,  $C_4H_7^\bullet$ , and  $C_4H_9^\bullet$ . These radicals are involved in the formation of main pyrolysis products. The production of  $1,3-C_4H_6$  is controlled by the reaction  $C_4H_7^\bullet \rightarrow C_4H_6 + H^\bullet$ . The rate constant for this reaction is independent of pressure and is given as a function of temperature by  $k = 2.2 \times 10^{13} \exp(-19.6 \times 10^3/T) s^{-1}$ . Production of  $C_2H_6$  is controlled by the reaction  $C_2H_5^\bullet + C_2H_4 \rightarrow C_2H_6 + C_2H_3^\bullet$ . The rate constant for this reaction is given as a function of temperature by  $k = 5.83 \times 10^{11} \exp(-14.6 \times 10^3/T) s^{-1}$ .  $C_3H_6$  is produced by decomposition of  $2-C_4H_9^\bullet$  and is controlled kinetically by the isomerization reaction  $1-C_4H_9^\bullet \rightarrow 2-C_4H_9^\bullet$ . The temperature dependence of the rate constants obtained for this reaction leads to a preexponential factor of approximately  $3 \times 10^{16}$  and an activation energy of approximately 200 kJ/mol. The yield of  $1-C_4H_8$  is controlled by the reaction  $1-C_4H_9^\bullet \rightarrow 1-C_4H_8 + H^\bullet$ . The rate constant for this reaction is independent of pressure and is given as a function of temperature by  $k = 2.97 \times 10^{12} \exp(-17.1 \times 10^3/T) s^{-1}$ .

Termination reactions typically lead to the formation of larger molecules that can undergo further decomposition with the formation of larger radicals. This route, similar to that of aliphatic hydrocarbons, explains, in part, the formation of heavier compounds (including PAHs) and ultimately of carbon in the form of soot [136]. The main mechanisms involved in ethylene pyrolysis below 1000 K are indicated in Table 7.3.1 with some characteristics of the reaction kinetics [137–142]. Some of the kinetic parameters from Table 7.3.1 were reported in the literature [137], and some were adjusted based on computer modeling of the pyrolysate composition as determined by flow through experiments [142].

Prolonged heating of ethylene leads to the formation of higher molecular weight compounds and of carbon (soot). Besides the reactions between radicals that lead to the formation of larger molecules, condensation reactions also are considered to play an important role in ethylene pyrolysis with the end result of high-molecular-weight compounds and of carbon. In these reactions, butadiene, cyclopentene, and cyclopentadiene play an important role. Some reactions leading to the formation of butadiene are shown in Table 7.3.1. Cyclopentene can be formed in the reaction:



Cyclopentene may further decompose with the formation of cyclopentyl radicals and further to cyclopentadiene. Cyclopentadiene also can be formed in reactions of the type:

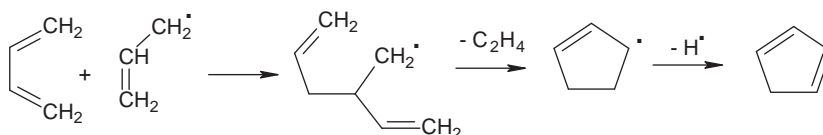


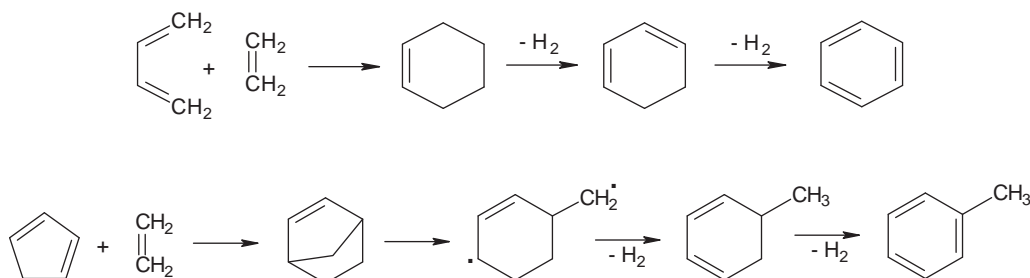
TABLE 7.3.1. Reactions involved in ethylene pyrolysis below 1000 K and some kinetic parameters of these reactions

Reaction	$A^*$	$\Delta E$ (kJ/mol)
<b>Initiations</b>		
$2 \text{ C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3^\bullet + \text{C}_2\text{H}_5^\bullet$	$1.02 \times 10^{12}$	269
$1\text{-C}_4\text{H}_8 \rightarrow \text{CH}_3^\bullet + \text{C}_3\text{H}_5^\bullet$	$5.00 \times 10^{14}$	287
$1\text{-C}_4\text{H}_8 \rightarrow \text{C}_2\text{H}_5^\bullet + \text{C}_2\text{H}_3^\bullet$	$1.30 \times 10^{14}$	290
<b>H-transfers</b>		
$\text{CH}_3^\bullet + \text{C}_2\text{H}_4 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_3^\bullet$	$6.30 \times 10^8$	67
$\text{C}_2\text{H}_5^\bullet + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_3^\bullet$	$3.23 \times 10^8$	62
$\text{H}^\bullet + \text{C}_2\text{H}_4 \rightarrow \text{H}_2 + \text{C}_2\text{H}_3^\bullet$	$8.55 \times 10^{10}$	51.2
<b>Additions</b>		
$\text{CH}_3^\bullet + \text{C}_2\text{H}_4 \rightarrow 1\text{-C}_3\text{H}_7^\bullet$	$3.31 \times 10^8$	32.2
$\text{C}_2\text{H}_5^\bullet + \text{C}_2\text{H}_4 \rightarrow 1\text{-C}_4\text{H}_9^\bullet$	$1.58 \times 10^8$	30.5
$1\text{-C}_4\text{H}_9^\bullet + \text{C}_2\text{H}_4 \rightarrow 1\text{-C}_6\text{H}_{13}^\bullet$	$2.34 \times 10^7$	28
$\text{C}_2\text{H}_3^\bullet + \text{C}_2\text{H}_4 \rightarrow \text{C}_4\text{H}_7^\bullet$	$2.70 \times 10^7$	30
$\text{H}^\bullet + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5^\bullet$	$2.64 \times 10^{10}$	9.04
$\text{C}_3\text{H}_5^\bullet + \text{C}_2\text{H}_4 \rightarrow \text{C}_5\text{H}_9^\bullet$	$1.81 \times 10^8$	60
<b>Radical decompositions</b>		
$1\text{-C}_3\text{H}_7^\bullet \rightarrow \text{CH}_3^\bullet + \text{C}_2\text{H}_4$	$3.00 \times 10^{14}$	139
$1\text{-C}_4\text{H}_9^\bullet \rightarrow \text{C}_2\text{H}_5^\bullet + \text{C}_2\text{H}_4$	$2.89 \times 10^{13}$	120
$2\text{-C}_4\text{H}_9^\bullet \rightarrow \text{CH}_3^\bullet + \text{C}_3\text{H}_6$	$3.72 \times 10^{14}$	138
$2\text{-C}_6\text{H}_{13}^\bullet \rightarrow 1\text{-C}_3\text{H}_7^\bullet + \text{C}_3\text{H}_6$	$1.58 \times 10^{13}$	118
$1\text{-C}_3\text{H}_7^\bullet \rightarrow \text{H}^\bullet + \text{C}_3\text{H}_6$	$1.00 \times 10^{14}$	156
$\text{C}_4\text{H}_7^\bullet \rightarrow \text{H}^\bullet + \text{C}_4\text{H}_6$	$3.16 \times 10^{13}$	146
$\text{C}_2\text{H}_3^\bullet \rightarrow \text{H}^\bullet + \text{C}_2\text{H}_2$	$3.12 \times 10^{13}$	189
$\text{C}_2\text{H}_5^\bullet \rightarrow \text{H}^\bullet + \text{C}_2\text{H}_4$	$1.59 \times 10^{13}$	156
$\text{C}_4\text{H}_7^\bullet \rightarrow \text{C}_2\text{H}_3^\bullet + \text{C}_2\text{H}_4$	$2.00 \times 10^{13}$	171
$1\text{-C}_4\text{H}_9^\bullet \rightarrow \text{H}^\bullet + \text{C}_4\text{H}_8$	$2.51 \times 10^{13}$	149
$1\text{-C}_6\text{H}_{13}^\bullet \rightarrow 1\text{-C}_4\text{H}_9^\bullet + \text{C}_2\text{H}_4$	$2.51 \times 10^{13}$	120
<b>Isomerizations</b>		
$1\text{-C}_4\text{H}_9^\bullet \rightarrow 2\text{-C}_4\text{H}_9^\bullet$	$2.09 \times 10^9$	85
$1\text{-C}_6\text{H}_{13}^\bullet \rightarrow 2\text{-C}_6\text{H}_{13}^\bullet$	$1.58 \times 10^9$	46
$\text{Acyclic-C}_5\text{H}_9^\bullet \rightarrow \text{cyclo-C}_5\text{H}_9^\bullet$	$2.00 \times 10^{11}$	75
<b>Terminations</b>		
$2 \text{ C}_2\text{H}_5^\bullet \rightarrow \text{C}_4\text{H}_{10}$	$1.08 \times 10^{10}$	0
$2 \text{ C}_2\text{H}_3^\bullet \rightarrow \text{C}_4\text{H}_6$	$9.60 \times 10^9$	0
$2 \text{ C}_2\text{H}_5^\bullet \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$	$1.39 \times 10^9$	0
$\text{C}_2\text{H}_3^\bullet + \text{C}_2\text{H}_5^\bullet \rightarrow 1\text{-C}_4\text{H}_8$	$1.60 \times 10^{10}$	0
$2 \text{ CH}_3^\bullet \rightarrow \text{C}_2\text{H}_6$	$1.67 \times 10^{10}$	-1.28

\*The frequency factor  $A$  is expressed in the appropriate units depending on the reaction order.



Ethylene with butadiene, as well as ethylene with cyclopentadiene, can react in Diels–Alder type condensations (or with radicalic mechanism) generating larger cyclic molecules including benzene [143]. Some of these reactions are indicated below:



Cyclopentene, cyclopentadiene, cyclohexene, cyclohexadiene, benzene, and toluene were detected during thermal decomposition of ethylene.

At temperatures around 1000 K, ethylene decomposition in the initial stages starts taking a different route to form higher levels of C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub> [144]. A study performed on ethylene highly diluted with neon in the temperature range of 1710–2170 K with reflected shock pressures of 225–1600 Torr generated mainly C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub> as well as some diacetylene [145]. The reactions involved in pyrolysis under these conditions are of the type:



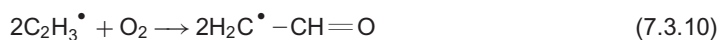
(where M is an inert molecule, which can be another ethylene molecule or the molecule of a diluent). Reaction 7.3.5 is either a simple unimolecular reaction or the result of the following sequence of reactions involving free radicals:



In the literature (e.g., [144]) are available extensive lists of reactions possibly involved in ethylene pyrolysis including their kinetic parameters (e.g., [140,146,147]). Some of these kinetic parameters were optimized using computer programs to account as close as possible for the experimental composition of pyrolysates.

Pyrolysis of ethylene in mixture with other compounds also has been studied, some of these studies having the goal of understanding the influence of ethylene on the pyrolysis of alkanes [66]. Pyrolysis of ethylene in the presence of catalysts has received considerable attention, mainly related to industrial production of light olefins [148].

Ethylene oxidation has been extensively studied in connection with pyrolysis, since the combustion of this compound starts with a pyrolytic process, similarly to the case of alkanes (see Section 7.1). The study of ethylene oxidation has been performed using different experimental setups [149–152], including shock tubes with the detection of resulting species by IR emission [150]. Formation of free radicals by pyrolysis is, as usual, the first step in combustion. The free radicals such as C<sub>2</sub>H<sub>5</sub><sup>•</sup> interact with oxygen in a manner already described for aliphatic hydrocarbons forming water and, as an intermediate, acetaldehyde, which is further oxidized to CO and CO<sub>2</sub>. The vinyl radicals, also formed by pyrolysis, generate more free radicals as well as ketene in reactions as shown below:



The hydroperoxyl, hydroxyl, and  $\text{CH}_2\text{CHO}^\bullet$  free radicals and ketene formation play an important role in the oxidation process of ethene. The modeling of the kinetics of flames of ethene is described in the literature [150,153]. The end products of combustion are CO,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ , with the  $\text{CO}/\text{CO}_2$  proportion depending on the  $\text{C}_2\text{H}_4/\text{O}_2$  ratio. Complete combustion with the formation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (gas) generates 316.2 kcal/mol.

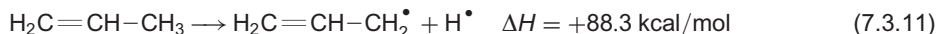
Formation of PAHs in ethylene flames was the subject of several studies [88,154,155] due to the interest in reducing the generation of these compounds during burning. It was determined that in the fuel lean flames, ethylene is almost completely converted into CO,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ , with virtually no formation of PAHs. In the fuel rich flames (with incomplete burning), the generation of vinyl radicals and subsequent formation of acetylene allows further formation of different aromatic species including PAHs (see Section 7.8).

### Propylene

Pyrolysis of propylene (propene) when heated between  $580^\circ\text{C}$  and  $640^\circ\text{C}$  at pressures between 40 Torr to 400 Torr in a static reactor generated  $\text{C}_2\text{H}_4$ ,  $\text{CH}_4$ , and  $\text{H}_2$  with lower amounts of  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , butenes, cyclopentadiene, cyclohexadiene, benzene, toluene, and 1,5-hexadiene [156]. At higher temperatures 1,2-propadiene or allene ( $\text{aC}_3\text{H}_4$ ), propyne ( $p\text{-C}_3\text{H}_4$ ),  $\text{C}_2\text{H}_2$ , and vinylacetylene are formed [157]. A more detailed analysis of the reaction products of the pyrolysis of propylene was done at temperatures between  $555^\circ\text{C}$  and  $640^\circ\text{C}$  at initial pressures between 7 Torr and 300 Torr [158]. In the study, 23 primary and 3 secondary products were identified at  $600^\circ\text{C}$  and an initial pressure of 103 Torr. These compounds included  $\text{C}_2\text{H}_4$ ,  $\text{CH}_4$ ,  $\text{H}_2$ , butenes, butadiene, methylcyclopentane, hexadienes, acetylene, and ethane, with secondary products cyclopentene, cyclopentadiene, and benzene. The overall reaction kinetics is described by the expression:

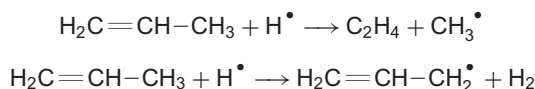
$$\frac{d[\text{C}_3\text{H}_6]}{dt} = 10^{14.06} [\text{C}_3\text{H}_6]^{1.4} \exp\left(\frac{-58600(\text{J})}{RT}\right) \text{ (appropriate units)}$$

Propene pyrolysis starts with an initiation reaction of the type:

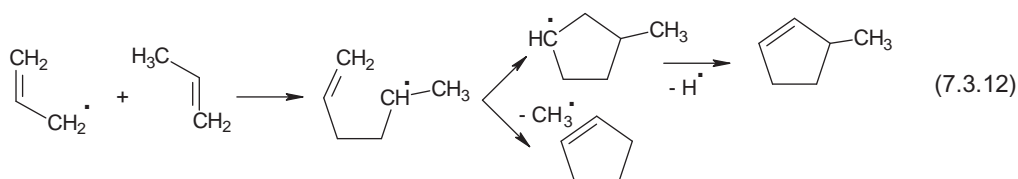


Although the heat of formation of allyl radical ( $\text{aC}_3\text{H}_5^\bullet$ ) is relatively high, 41 kcal/mol ( $39.7 \pm 1.0$  kcal/mol as reported in [159]), this radical seems to be stabilized by the delocalization of the unpaired electron and  $\pi$  electrons of the double bond.

The free radicals formed during the initiation undergo further propagation reactions, as shown below for the hydrogen atoms:



The presence of  $\text{H}^\bullet$  and  $\text{CH}_3^\bullet$  radicals explains the formation of hydrogen, methane, ethane, etc. The allyl radical can lead to the generation of propynyl radicals ( $p\text{-C}_3\text{H}_3^\bullet$ ) that further can form propyne. Also, typical for propene pyrolysis compared to that of ethylene (besides higher conversion at lower temperatures) is the formation of larger proportions of cyclopentene, cyclopentadiene, methylcyclopentane, and methylcyclopentene. This result can be explained by the high content (and stability) of allyl radical formed in the initial stages of pyrolysis and the participation in reactions of the type:

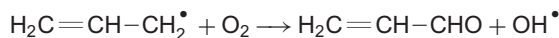
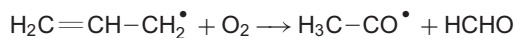
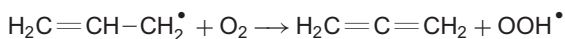


Besides shorter-chain molecules, the pyrolysate of propene contains 1,3- and 1,4-hexadiene, leading to the conclusion that 1-methyl-4-pentenyl radical plays an important role during pyrolysis. At temperatures between 703 °C and 845 °C, the main products of pyrolysis are C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, and H<sub>2</sub>, butenes (1-butene being a major component), butadiene, methylcyclopentane, hexadienes, acetylene, and ethane, with secondary products cyclopentene, cyclopentadiene, benzene, toluene, and higher molecular weight aromatic compounds. Trace amounts of propane, 1,2-propadiene, methylacetylene, cyclohexane, cyclohexadiene, 4-methylcyclohexane, xylenes, and styrene also have been detected in the pyrolysate [160,161]. The comparison of the pyrolysates composition at 600 °C [158] and 800 °C [161] shows that except for the higher amount of ethane and acetylene, there is no significant difference in the two pyrolysates. With the increased conversion of propene, the level of very low-molecular-weight compounds (H<sub>2</sub>, CH<sub>4</sub>) and of aromatics (benzene, condensed aromatics) increases, while the level of middle range compounds (C<sub>4</sub>, C<sub>5</sub>) decreases.

Various other studies regarding pyrolysis of propylene were performed. One such study used theoretical evaluation based on density functional theory of heat capacities, entropies, enthalpies of formation, and Gibbs free energies of formation for propylene pyrolysis components in gas-phase reactions [162]. Based on the calculated data, the equilibrium concentration distribution for all of the species in the temperature range of 100–1500 K were calculated according to the chemical equilibrium principle. Other studies evaluated the influence on propylene pyrolysis of the active sites of deposited carbon [163,164], pyrolysis and oxidation of propylene [165], and pyrolysis in the presence of other hydrocarbons such as propane [166].

One subject related to propene pyrolysis is the capability of allyl radical formed in propene pyrolysis to react with various olefins. This type of reaction takes place when mixtures of olefins including propene are subject to pyrolysis. However, since propene pyrolysis generates besides allyl other free radicals, such as hydrogen atoms (see reaction 7.3.11), several studies were performed using diallyl oxalate as a source of allyl radicals. This compound upon heating generates CO<sub>2</sub> and allyl radicals. It was demonstrated that the allyl radical reacts with various alkenes, alkadienes, and alkynes, generating both acyclic and cyclic compounds, including cyclopentene, substituted cyclopentenenes, cyclopentadiene, cyclohexene, cyclohexadiene, and benzene [167]. The study proved the role of allyl radicals in the formation of aromatic compounds during pyrolysis.

Propene pyrolysis and oxidation in flames has been the subject of several studies [168–171]. Similar to the case of other hydrocarbons, propene combustion starts with the formation of free radicals due to pyrolysis. The process consists of numerous reactions (287 possible reactions were considered for modeling propene pyrolysis in a study of oxidation kinetics in a flow reactor and in laminar flames [169]). Among the most common ones are those involving the allyl radical:



Various other pyrolysis products of propene such as propyne and allene may be involved in the combustion process. Formation of oxygen atoms during heating ( $\Delta H = 35 \text{ kcal/mol}$  for oxygen) and direct reaction with propene is possible.

### Butenes and isobutene

Butenes include two position isomers, namely 1-butene and 2-butene, with 2-butene having a *cis*- and a *trans*-form. Thermal decomposition of butenes in the range of 640–680 °C generates mainly propene, methane, ethene, and butadiene. Each butene also generates some of the other butene isomers. The variation in the composition of pyrolysate as a function of mole percent conversion for 1-butene is shown in Figure 7.3.3. The same graph for *cis*-2-butene is shown in Figure 7.3.4, and the one for *trans*-2-butene is shown in Figure 7.3.5 [128].

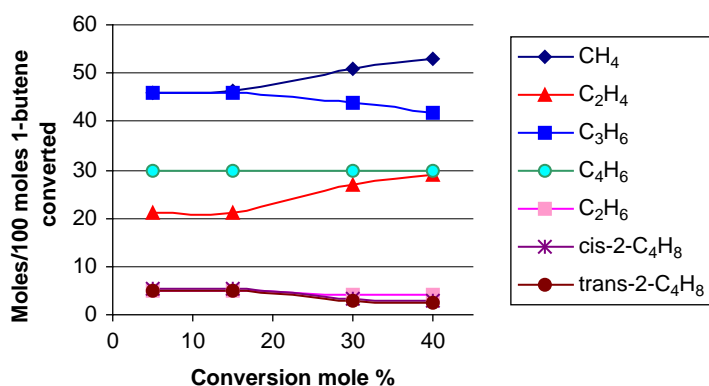


FIGURE 7.3.3. Variation in the composition of 1-butene pyrolysate as a function of mole conversion percent.

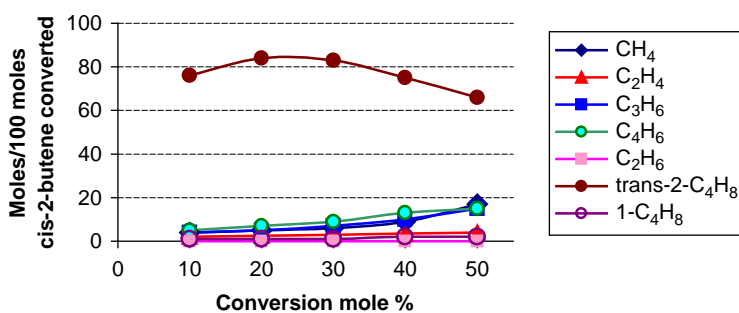


FIGURE 7.3.4. Variation in the composition of cis-2-butene pyrolysate as a function of mole conversion percent.

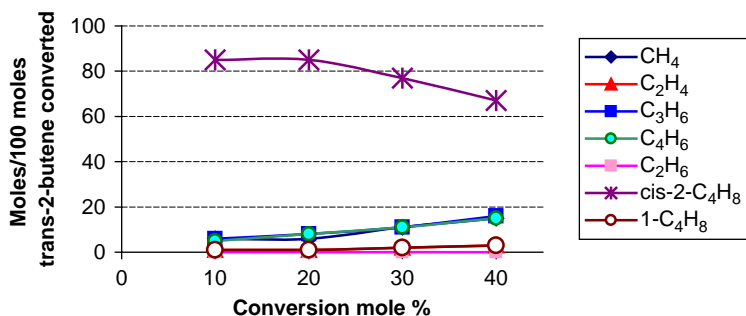
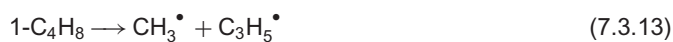


FIGURE 7.3.5. Variation in the composition of trans-2-butene pyrolysate as a function of mole conversion percent.

Although the nature of pyrolysis products is similar for the three butenes, considerable differences can be noticed between the percent mole compositions of their pyrolysates. The decomposition of 1-butene is dominated by the formation of small molecules including methane and ethane; 2-butenes show practically no ethane formation; and methane and propane are present at considerably lower levels than in 1-butene pyrolysate. The initiation step has a simple free radical mechanism of the form:



The rate constant for the initial rate-limiting step reaction has the form [172]:

$$k = 5 \times 10^{14} \exp\left(\frac{-287(\text{kJ/mol})}{RT}\right) \text{s}^{-1} \quad (7.3.14)$$

The pyrolysis of 1-butene also generates heavier compounds. The allyl radical  $\text{CH}_2=\text{CH}-\text{CH}_2^\bullet$  formed in butane pyrolysis easily reacts with the undecomposed butene, leading to higher molecular weight compounds. The formation of  $\text{C}_5$  species starts at about  $625^\circ\text{C}$ , and of  $\text{C}_6$  species starts at about  $650^\circ\text{C}$ . At temperatures of  $675\text{--}700^\circ\text{C}$ , the amount of  $\text{C}_5$  gradually decreases while the amount of  $\text{C}_6$  continues to increase.

The homogeneous pyrolysis of 2-butene subjected to shock heating over the temperature range of  $1150\text{--}1325\text{ K}$  indicates that practically equal amounts of methane, propylene, and butadiene with traces of hydrogen are formed from either the *cis*- or *trans*-2-butene, and isomerization does not reach equilibrium. The results are consistent with a simple free radical mechanism starting with an initiation of the form:



The rate constant for the initial rate-limiting step reaction has the form [172]:

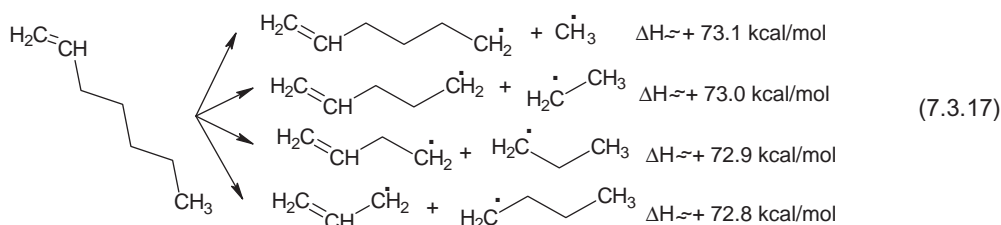
$$k^\infty = 10^{16} \exp\left(\frac{-80000(\text{J/mol})}{RT}\right) \text{s}^{-1} \quad (7.3.16)$$

Isobutene (isobutylene)  $(\text{CH}_3)_2\text{C}=\text{CH}_2$  does not show significant pyrolytic reactions until  $675^\circ\text{C}$ , which is a temperature significantly higher than that for the decomposition of other  $\text{C}_4$  species. The main products of pyrolysis are  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ , and isomers of  $\text{C}_4$ . The  $\text{C}_5$  and  $\text{C}_6$  species start forming around  $700^\circ\text{C}$ , where the conversion of isobutene is still very low. The process continues until around  $750^\circ\text{C}$  when the amount of  $\text{C}_5$  starts decreasing while the amount of  $\text{C}_6$  continues to increase.

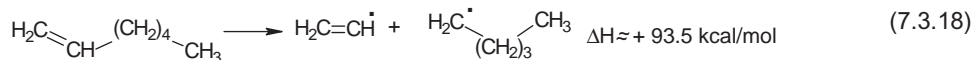
Catalytic pyrolysis of butenes is influenced, as expected, by the temperature, dilution with inert gases, and the nature of the catalyst. On a modified ZSM-5 zeolite, pyrolysis mechanism of butene involves a bimolecular reaction mechanism with a dimerization first step followed by the cracking of the dimers [173]. Various practical applications of butenes pyrolysis are reported in the literature [174,175].

### Higher molecular weight alkenes

Long-aliphatic-chain alkenes generate a pyrolysate very similar to the long-aliphatic-chain alkanes. However, there are some differences in the pyrolysis mechanisms of alkanes and alkenes. For similar mechanisms, 1-alkenes should generate by pyrolysis considerable levels of shorter  $1,n$ -alkadienes. However, only slightly higher levels of these compounds are noticed in the pyrolysates of 1-alkenes as compared to the levels in the pyrolysates of the homolog 1-alkanes. The initiation step in pyrolysis is dominated, as usual for hydrocarbons, by the formation of free radicals. Various possible initiation reactions during pyrolysis are exemplified below for 1-heptene:

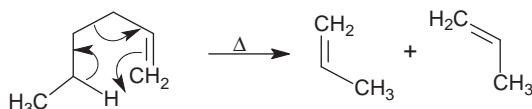


The formation of vinyl free radical is less favorable thermodynamically, as seen from the variation in the enthalpy of this reaction:



(Not only the enthalpy but also the free enthalpy  $\Delta G$  of reaction 7.3.18 should be higher than for reactions 7.3.17, and therefore, thermodynamically, reaction 7.3.18 is not favored.)

At very low pressures and lower temperature, besides the radicalic mechanism, the pyrolysis occurs also with a retro-ene mechanism shown below for 1-hexene [176]:



However, the radicalic mechanism is dominant at higher temperatures. As shown in Section 7.1,  $\beta$ -scissions of the alkyl free radicals led to the formation of 1-alkenes (see reaction 7.1.50). However, the alkenyl radicals should generate by the same mechanism 1,*n*-alkadienes. This conclusion is not fully demonstrated by the experimental results obtained in the pyrolysis of several long-chain 1-alkenes. As an example, Figure 7.3.6 shows the pyrogram of 1-pentadecene. The pyrolysis was performed under flash condition from 0.2 mg material using Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ , and analyzed under conditions given in Table 4.6.1. The peak identification is given in Table 7.3.2. A considerable amount of sample vaporizes under the selected pyrolysis conditions.

The comparison of the pyrogram shown in Figure 7.3.6 with that from Figure 7.1.11 shows very good similarity regarding the nature of the generated compounds (the small differences in the retention times of peaks generated by the same compound in pyrograms from Figures 7.1.11 and 7.3.6 are caused by instrumental variability). The relative content in the pyrolysate of different components is similar, having the 1-alkenes dominating the pyrogram.

As can be seen from Table 7.3.2, although the 1,*n*-alkadienes are present in the pyrolysate, they are not at equal (or close) level with the 1-alkenes. This is an indication that the alkenyl free radicals

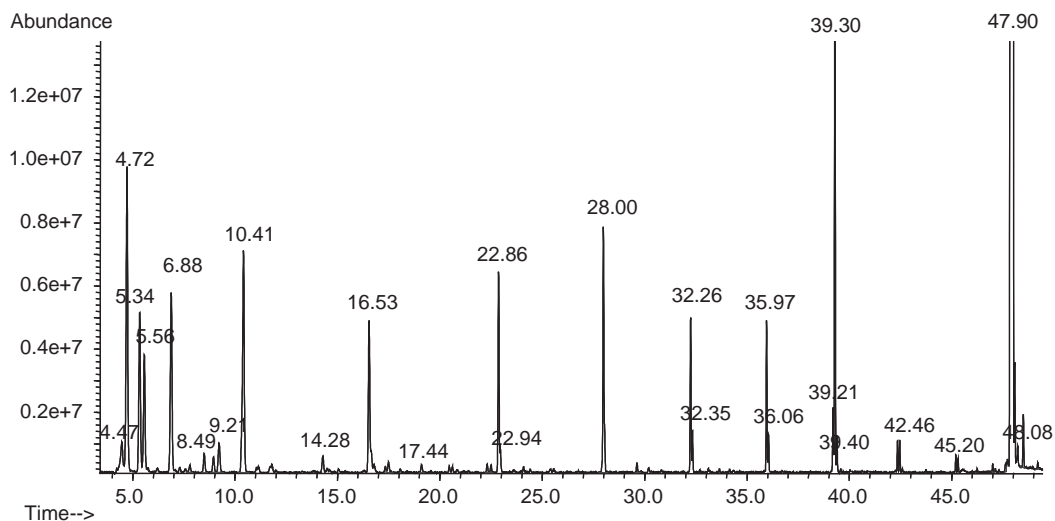


FIGURE 7.3.6. Pyrogram of 1-pentadecene ( $\text{C}_{15}\text{H}_{30}$ ) at  $900^\circ\text{C}$ . Peak assignment given in Table 7.3.2.

TABLE 7.3.2. Peak identification in the pyrogram shown in Figure 7.3.6 for the pyrolysis of 1-pentadecene (hydrogen, methane, and ethylene were not analyzed due to the mass spectrometer settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Ethene	4.47	30	74-84-0	5.62
2	Propene	4.72	42	115-07-1	<b>25.63</b>
3	1-Butene	5.34	56	106-98-9	<b>9.96</b>
4	1,3-Butadiene	5.56	54	106-99-0	7.24
5	1-Pentene	6.88	70	109-67-1	<b>9.45</b>
6	2-Methyl-1-butene	7.28	70	563-46-2	Trace
7	3-Methyl-1-butene	7.53	70	536-45-1	Trace
8	1,2-Pentadiene	7.78	68	591-95-7	Trace
9	Isoprene	8.49	68	78-79-5	0.97
10	1,3-Pentadiene	8.94	68	504-60-9	0.79
11	1,3-Cyclopentadiene	9.16	66	542-92-7	Trace
12	Cyclopentene	9.21	68	142-29-0	1.72
13	1-Hexene	10.41	84	592-41-6	<b>10.60</b>
14	Hexane	11.01	86	110-54-3	Trace
15	3-Methylcyclopentene	14.28	98	1120-62-3	0.57
16	1-Heptene	16.53	98	592-76-7	<b>4.10</b>
17	Cyclohexene	16.64	82	110-83-8	0.71
18	Cyclohexadiene	16.80	80	592-57-4	0.29
19	1,5-Heptadiene	17.32	96	7736-34-7	Trace
20	Benzene	17.44	78	71-43-2	Trace
21	1-Octene	22.86	112	111-66-0	<b>4.17</b>
22	1,7-Octadiene	22.94	110	3710-30-3	0.44
23	1-Nonene	28.00	126	124-11-8	<b>4.69</b>
24	1-Decene	32.26	140	872-05-9	<b>2.10</b>
25	Ethenylcyclohexane	32.35	110	695-12-5	0.71
26	1-Undecene	35.97	154	821-95-4	<b>1.82</b>
27	1,10-Undecadiene	36.06	152	13688-67-0	0.46
28	<i>n</i> -Dodecane	39.21	170	112-40-3	0.72
29	1-Dodecene	39.30	168	112-41-4	<b>5.96</b>
30	1,11-Dodecadiene	39.40	166	5876-87-9	0.41
31	1-Tridecene	42.36	182	2437-56-1	<b>0.30</b>
32	1,13-Tridecadiene	42.46	180	21964-49-8	0.31
33	1-Tetradecene	45.20	196	1120-36-1	<b>0.15</b>
34	1,13-Tetradecadiene	45.31	194	21964-49-8	0.12
35	Pentadecane	47.80	210	629-62-9	Trace
36	1-Pentadecene	47.90	212	13360-61-7	Not included

Note: 1-alkene moles % values are written with bold characters.

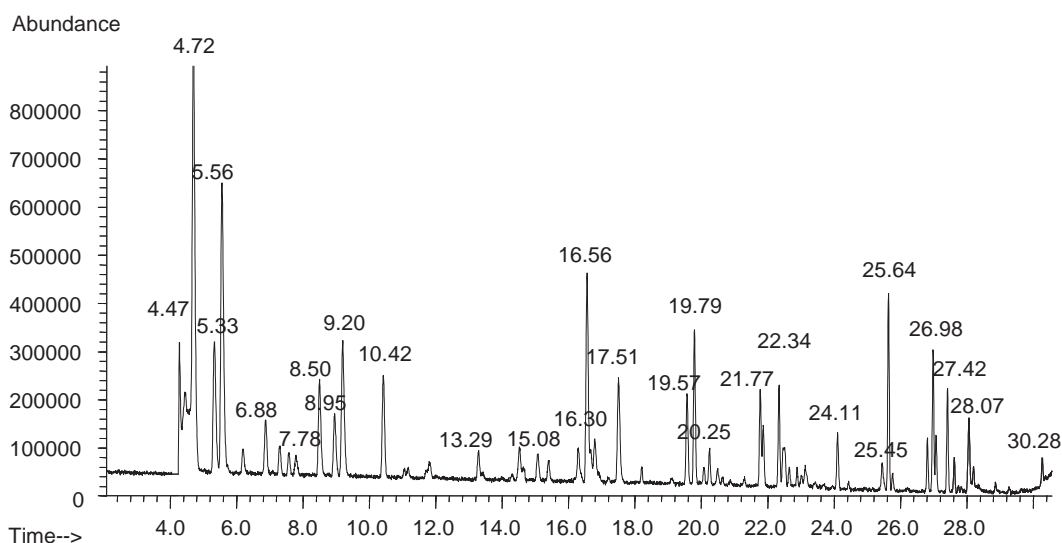
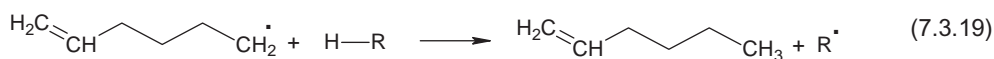


FIGURE 7.3.7. Pyrogram of *trans*-5-decene ( $C_{10}H_{20}$ ) at 900 °C. Peak assignment given in Table 7.3.3.

undergo hydrogen abstraction reactions much more frequently than the alkyl radicals. These reactions are of the type:



For the same chain length the enthalpy of formation  $\Delta H$  (at standard temperature) of the alkyl radicals is about 20 kcal/mol lower than that for the alkenyl radical ( $\Delta H$  values for vinyl and ethyl radical differ by 40 kcal/mol). This would highly favor the hydrogen abstraction reaction 7.3.19 and the formation of 1-alkenes.

When the double bond in the initial alkene is not in 1-position, the molecule will form a variety of radicals in the initiation reaction. These radicals will follow reactions similar to those generated from 1-alkenes. An example of a pyrogram for an alkene with the double bond in 5-position is given in Figure 7.3.7 for *trans*-5-decene. The pyrogram was obtained from 0.13 mg material. The pyrolysis was performed under flash condition using Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900$  °C,  $\beta = 10$  °C/ms, THT = 10 s, with housing temperature  $T_{hou} = 280$  °C, and the pyrolysate was analyzed under conditions given in Table 4.6.1. The peak identification is given in Table 7.3.3.

The pyrogram contains a variety of compounds besides 1-alkenes, with relatively high levels of cyclic alkenes. 5-Decene also was found in the pyrolysate. The formation of 1-alkenes is no longer the characteristic feature of the pyrolysis.

### Other alkenes

The influence of heat at temperatures above 350–400 °C was studied on a variety of other alkenes. Besides decomposition, one interesting reaction noticed in some of these compounds is the migration of the double bond. A typical rearrangement is seen, for example, for 3-methyl-1-butene, which around 515 °C is transformed with a rate of about 33% into 2-methyl-2-butene as shown below:

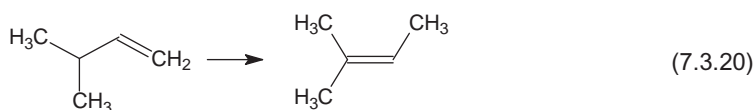




TABLE 7.3.3. Identification of the main peaks in the chromatogram shown in Figure 7.3.7 for the pyrolysis of *trans*-5-decene (hydrogen, methane, and ethylene were not analyzed due to the mass spectrometer settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Ethene	4.47	30	74-84-0	6.98
2	Propene	4.70	42	115-07-1	<b>24.33</b>
3	1-Butene	5.33	56	106-98-9	<b>4.91</b>
4	Butadiene	5.56	54	106-99-0	9.84
5	1,1-Dimethylcyclopropane	6.19	70	1630-94-0	0.83
6	1-Pentene	6.88	70	109-67-1	<b>1.67</b>
7	2-Methyl-1-butene	7.29	70	563-46-2	1.02
8	3-Methyl-1-butene	7.58	70	536-45-1	0.68
9	1,2-Pentadiene	7.78	68	591-95-7	Trace
10	Isoprene	8.50	68	78-79-5	2.68
11	1,3-Pentadiene	8.95	68	504-60-9	1.87
12	1,3-Cyclopentadiene	9.20	66	542-92-7	3.96
13	1-Hexene	10.42	84	592-41-6	<b>2.44</b>
14	1,3-Hexadiene	13.29	82	592-48-3	0.54
15	1-Methyl-1,3-cyclopentadiene	14.52	80	96-39-9	0.94
16	1,3-Cyclohexadiene	15.08	80	529-57-4	0.63
17	1-Methylcyclopentene	15.37	82	693-89-0	Trace
18	2,4-Hexadiene	16.30	82	6108-61-8	1.04
19	1-Heptene	16.56	98	592-76-7	<b>3.82</b>
20	3-Methylen-cyclopentene	16.79	80	N/A	<b>0.69</b>
21	Benzene	17.51	78	71-43-2	2.56
22	2-Heptene	18.21	98	592-77-8	<b>Trace</b>
23	Vinylcyclopentane	19.57	96	3742-34-5	1.49
24	Cycloheptene	19.79	96	628-92-2	2.14
25	2-Ethyl-1-hexene	20.25	112	1632-16-2	0.53
26	2,4-Dimethyl-1,3-pentadiene	21.78	96	1000-86-8	1.33
27	2,3-Dimethyl-1,3-pentadiene	21.87	96	1113-56-0	0.85
28	4-Methyl-1,4-hexadiene	22.34	96	1116-90-1	1.30
29	2-Methyl-2,4-hexadiene	22.51	96	28823-41-8	0.96
30	1-Octene	22.86	112	111-66-0	Trace
31	3-Methyl-1,3,5-hexatriene	23.00	94	24587-27-7	Trace
32	Toluene	24.11	92	108-88-3	0.74
33	Vinylcyclohexene	25.45	110	695-12-5	0.48
34	1,3-Octadiene	25.64	110	1002-33-1	1.90
35	1,4-Octadiene	25.76	110	5675-25-2	Trace
36	3,5-Octadiene	26.81	110	7348-80-3	0.58
37	1-Ethylcyclohexene	26.98	110	1453-24-3	1.48
38	2,4-Octadiene (2 <i>E</i> ,4 <i>E</i> ?)	27.07	110	13643-08-8	0.61
39	2,4-Octadiene (2 <i>E</i> ,4 <i>Z</i> ?)	27.42	110	13643-08-8	1.06
40	2,4-Octadiene (2 <i>Z</i> ,4 <i>Z</i> ?)	27.63	110	13643-08-8	0.39
41	1,3-Nonadiene	28.21	124	56700-77-7	0.23
42	2-Methylocta-1,3-diene	30.27	124	N/A	0.29
43	<i>cis</i> -5-Decene*	31.67	140	19398-89-1	6.29
44	5-Decene	32.34	140	7433-56-9	Not included
45	5-Decene	34.68	138	1942-46-7	5.94

\*A part of *cis*-5-decene from the pyrolysate may be an impurity in the starting material taken for pyrolysis.

Similar reactions are seen for other compounds when the resulting molecule is more stable to heat. In the case of reaction 7.3.20, the cleavage of a C–C bond where one of the carbons is involved in a double bond (has  $sp^2$  hybridization) occurs with more difficulty as compared to the case when both carbons have  $sp^3$  hybridization.

## 7.4. ALKADIENES AND POLYENES

### General aspects

Alkadienes are hydrocarbons containing two double bonds between carbon atoms. These two double bonds can be present in the molecule at different positions, connected to the same carbon atom (cumulated,  $C=C=C$ ), separated from each other by a single  $\sigma$  bond (conjugated,  $C=C-C=C$ ), or separated by one or more carbons with  $sp^3$  hybridization (isolated). The compounds with cumulated or conjugated double bonds, which influence each other, have properties different from compounds with isolated double bonds. Isolated double bonds do not have any significant influence on each other, and the compounds containing them behave very similarly to alkenes.

In a hydrocarbon with cumulated double bonds (such as allene  $CH_2=C=CH_2$ ), the central carbon has an  $sp$  hybridization, and only the two terminal carbons have  $sp^2$  hybridization. This is the cause of the differences between alkenes that have carbons with only  $sp^2$  hybridization and allenes. The conjugated double bonds also have special properties, the system behaving in many instances as a distinct unit and not as two separated double bonds. This is caused by the delocalization of the  $\pi$  electrons along the  $sp^2$  hybridized orbitals of the four carbon atoms forming the conjugated system. The lowest hydrocarbon with conjugated double bonds, namely 1,3-butadiene ( $H_2C=CH-CH=CH_2$ ) is a very important industrial product, and 2-methyl-1,3-butadiene (isoprene) also has industrial importance and is the structural unit for a large class of natural products known as terpenes.

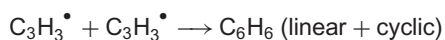
Terpene hydrocarbons include a hemiterpene (isoprene), monoterpenes that are formed from two isoprene units and have the formula  $C_{10}H_{16}$ , sesquiterpenes ( $C_{15}H_{24}$ ), diterpenes ( $C_{20}H_{32}$ ), sesterterpenes ( $C_{25}H_{40}$ ), triterpenes ( $C_{30}H_{48}$ ), tetraterpenes ( $C_{40}H_{56}$ ), etc. Related to the terpenes are numerous other compounds commonly known as terpenoids. These compounds may have different arrangements of the isoprene units (e.g., squalene with the formula  $C_{30}H_{50}$ ) or may contain cycles, additional double bonds, aromatic rings, alcohol, aldehyde, ketone, as well as other functional groups. Terpenoids include special classes of compounds such as carotenoids and steroids.

Other compounds with more than two double bonds in the molecule, indicated as polyenes, are also present in nature. Polyene chains also are present in compounds that contain other functional groups (such as some fatty acids, prostaglandins, and isoprostanes). Pyrolysis of terpenoids and polyenes with additional functionalities will be discussed in various sections of this book, depending on their specific functional groups.

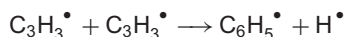
### Allenes

1,2-Propadiene and its homologs (allenes) are not common compounds (1,2-propadiene is also named allene). Pyrolysis of allene is associated with its isomerization to propyne. Different allenes may be formed during pyrolysis of propene and of other hydrocarbons (see Section 7.3). Allene molecules are probably involved in the combustion process of propene, butadiene, etc. [177]. 1,2-Butadiene, the next homolog of allene, is a typical isomerization product of 1,3-butadiene during pyrolysis. Its own pyrolysis generates in the initial phases free radicals such as  $CH_3^\bullet$  and  $C_3H_3^\bullet$  (propargyl) followed by secondary reactions that produce pyrolysates with a composition similar to that of 1,3-butadiene [178].

1,2,4,5-Hexatetraene ( $CH_2=C=CH-CH=C=CH_2$ ) is considered a key intermediate to benzene from propargyl radicals ( $CH\equiv C-CH_2^\bullet$ ). Separate studies on propargyl radical decomposition and bimolecular recombination showed that the main route for the bimolecular reaction is the direct recombination to linear and/or aromatic  $C_6H_6$ -species:



The benzene fraction among other products increases with temperature. The reaction leading directly to phenyl by the reaction:



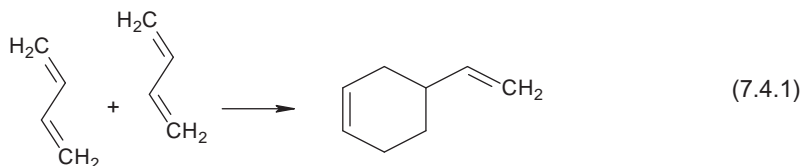
was found to proceed with a rate constant of less than 10% of the total reaction rate [179].

1,2,4,5-Hexatetraene was pyrolyzed in a single-pulse shock tube at two nominal pressures of 22 and 40 bar over a temperature range from 540 K to 1180 K [180]. At temperatures lower than 700 K, the compound converts efficiently to 3,4-dimethylene-cyclobutene with a rate constant of  $k = 10^{10.16} \exp[-23.4 \text{ (kcal/mol)/}RT] \text{ s}^{-1}$ . At higher temperatures, various  $\text{C}_6\text{H}_6$  isomers were generated including benzene, 1,2-hexadien-5-yne, 2-ethynyl-1,3-butadiene, and fulvene. The result supports the theory that 1,2,4,5-hexatetraene plays a role in the formation of benzene from propargyl radicals.

### 1,3-Butadiene and isoprene

1,3-Butadiene is typically obtained industrially by pyrolytic reactions from the  $\text{C}_4$  fraction of oil processing products. Since butadiene is a valuable industrial material, its pyrolysis has been studied mainly with the purpose of determining the best ways to avoid its thermal decomposition. These studies have been performed under different conditions such as with inert diluents, including temperatures below 1000 K [181–183], as well as with higher temperatures [178,184–187].

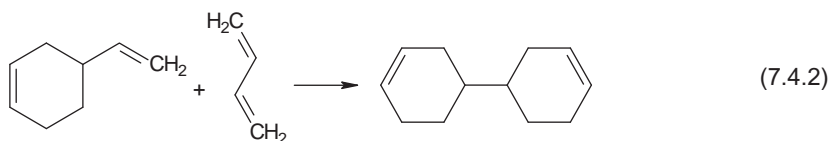
Below 700 K the main reaction that takes place upon heating of butadiene is the formation of 4-vinylcyclohexene in a Diels–Alder reaction shown as follows:



The reaction has a second order kinetics with the rate constant given by the expression [188]:

$$k = 10^{9.96} \exp\left(\frac{-23708(\text{cal})}{RT}\right) \text{ cm}^3/\text{mol/s}$$

Since Diels–Alder reactions are not favored by the increase in temperature because the entropic term in the expression of free enthalpy becomes more unfavorable for Diels–Alder condensation, reaction 7.4.1 also can take place by a radicalic mechanism. Small amounts of 4,4'-octahydrobiphenyl are also formed during heating by further condensation of 4-vinylcyclohexene with butadiene:



At temperatures above 700 K, the pyrolysis products of butadiene begin to include cyclohexane, cyclohexadiene, benzene, butenes, propylene, ethylene, methane, vinylacetylene, and hydrogen.

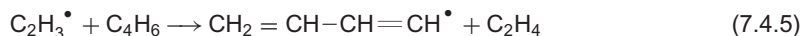
At temperatures above 1000 K, the thermal decomposition has a radicalic mechanism. The main initiation reaction is the formation of vinyl radicals:



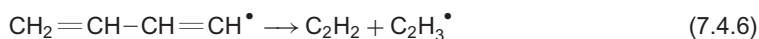
The heat of formation for reaction 7.4.3 is indicated for 278.3 K, and using the heat of formation for the vinyl radical  $\Delta H = +69$  kcal/mol [189]. For temperatures where pyrolysis occurs, this value can be somewhat different. At temperatures between 1600 K and 1900 K, the reaction rate for reaction 7.4.3 was found to fit the expression [187]:

$$k^\infty = 4.1 \times 10^{16} \exp\left(\frac{-47000}{T}\right) \text{ s}^{-1} \quad (7.4.4)$$

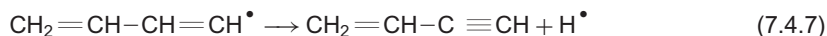
Following the initiation reaction, various secondary processes take place during butadiene pyrolysis. Among the pyrolysis products at higher temperatures, the main products are ethylene and acetylene in about equal quantities. The mechanism for this reaction seems to be the following:



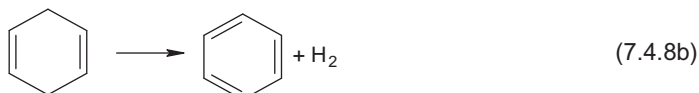
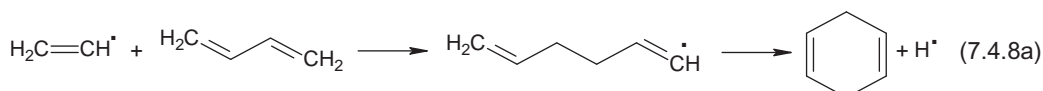
with the fast decomposition of the radical  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}^\bullet$  (also indicated as  $n\text{-C}_4\text{H}_5^\bullet$ ) generating acetylene by the reaction:



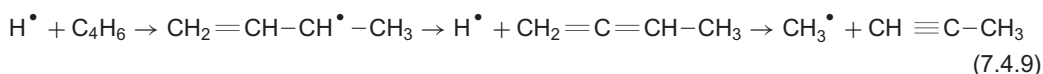
Besides ethylene and acetylene, the other compounds formed above 1200 K, although at considerably lower levels, are vinylacetylene and benzene. The formation of vinylacetylene can be explained by the generation of  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}^\bullet$  radical, which participates in the reaction:



The addition of vinyl radical to a butadiene molecule is probably involved in the formation of benzene by the sequence of reactions:

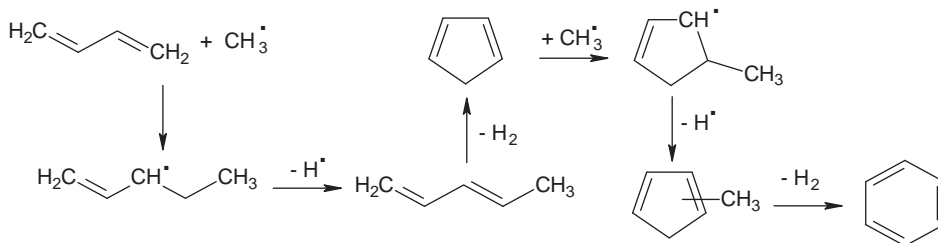


Other dissociation paths are not excluded at high temperatures, including the formation of  $\text{CH}_2=\text{C}^\bullet-\text{CH}=\text{CH}_2$  (also indicated as  $i\text{-C}_4\text{H}_5^\bullet$ ) and of  $\text{H}^\bullet$  radicals by the dissociation of a C–H bond with a dissociation energy of about 15 kcal/mol lower than that of the C–C bond. The radical  $\text{CH}_2=\text{C}^\bullet-\text{CH}=\text{CH}_2$  ( $i\text{-C}_4\text{H}_5^\bullet$ ) may be stabilized by delocalization between the unpaired electron and the  $\pi$  electrons of the conjugated double bond. Other reactions take place during pyrolysis, explaining the formation of various minor components of butadiene pyrolysates at temperatures above 1000 K up to 1900 K [187]. For example, hydrogen atoms may react with butadiene in the following series of reactions:



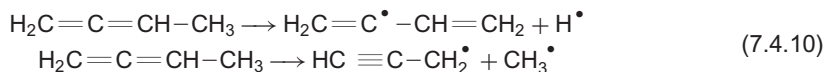
The methyl radicals may react further to generate methane, ethane, propene, 1,3-pentadiene, etc. As an example, the reaction chain starting with butadiene and methyl radical and continuing with the

formation of cyclopentadiene and further of benzene is shown below:

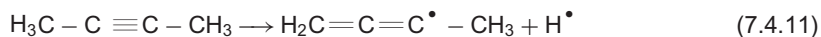


In conclusion, butadiene thermal decomposition is a complex process, and the role of different reactions depends on temperature, but the end result is a complex mixture containing aromatic compounds including PAHs.

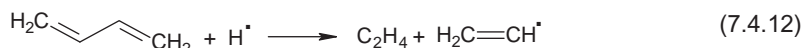
Alternative mechanisms have been proposed for butadiene pyrolysis. The isomerizations of 1,3-butadiene to 1,2-butadiene, to 1-butyne, or to 2-butyne were found to be rapid processes with a relatively low energy barrier (about 85 kcal/mol) [190,191]. These isomerizations require energies considerably lower than that of the cleavage of a C–C or C–H bond in butadiene. These isomers could be generated initially during heating, themselves undergoing further thermal decomposition. The decomposition of 1,2-butadiene will take place, for example, after free radicals formation and isomerizations, with the generation of free radicals such as  $\text{H}^\bullet$  and  $\text{CH}_3^\bullet$ , as shown below:



The intermediate compound 2-butyne also decomposes as follows:

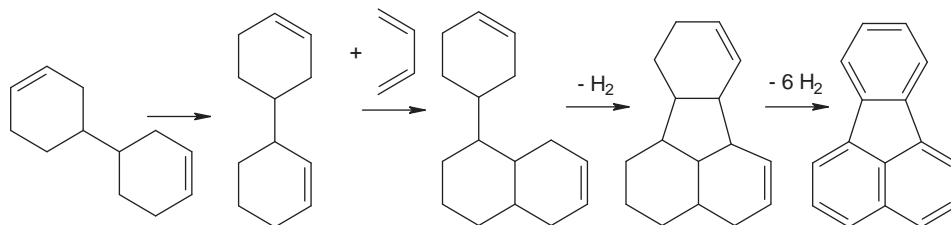


The hydrogen atoms generated in these reactions can react further with butadiene as shown below:



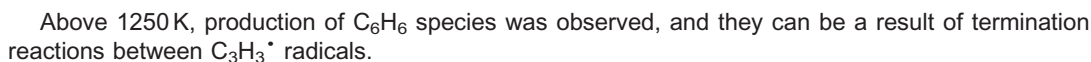
These alternative mechanisms do not explain well the presence of large and equal amounts of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  in the initial stages of pyrolysis of butadiene, which indicates that reaction 7.4.3 can be considered the main initiation mechanism.

The materials generated by prolonged pyrolysis of butadiene (and those obtained from incomplete combustion of butadiene) were found to have a considerable cytotoxic and genotoxic effect on human cells [192] and to contain a variety of PAHs. The capability to undergo Diels–Alder condensations (or similar condensation by radicalic mechanisms) makes 1,3-butadiene prone to the production of this class of compounds (see Section 7.8). More than one reaction path is probably responsible for this result. One such path is, for example, the continuation of the condensation of butadiene with 4,4'-octahydrobiphenyl generated in reaction 7.4.2. Isomerizations, further condensations, and several steps of dehydrogenation can lead to the formation of fluoranthene:



Various studies were performed on pyrolysis of butadiene in mixture with other olefins such as ethylene and propylene. At temperatures between 510 °C and 670 °C, the condensations take place

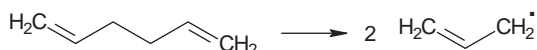
Butadiene oxidation is a process that may or may not involve pyrolysis [193]. The early phase of reaction may involve only a reaction with oxygen atoms that are generated by heat (the bond energy for the oxygen molecule is only 35 kcal/mol), as follows:



### 1,5-Hexadiene and 1,7-octadiene

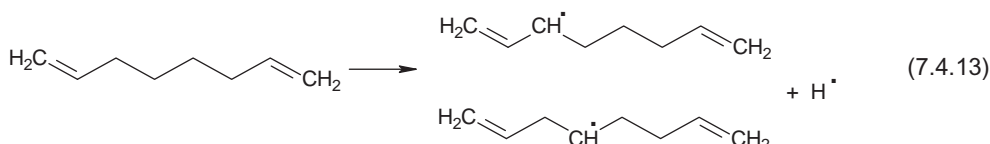
Pyrolysis of  $\alpha,\omega$ -alkadienes (with separated double bonds) typically takes place with the formation of free radicals by the cleavage of a C–C  $\sigma$  bond. For example, 1,5-hexadiene at 500–620 °C generates a number of compounds with two to six carbon atoms in the relative ratio shown in Figure 7.4.1 [196].

The main initiation reaction during 1,5-hexadiene pyrolysis is probably the formation of allyl radicals as shown below:



The allyl radicals undergo further reactions to form various pyrolysis products (see Section 7.3). Numerous secondary reactions follow this initial step, which explains the generation of a variety of compounds. In later stages of pyrolysis, aromatic compounds such as benzene are detected in the pyrolysate.

1,7-Octadiene is a primary product from the pyrolysis of *cis*-decalin (see Section 7.2). The activation energy of 1,7-octadiene pyrolysis is about 43 kcal/mol [118]. At temperatures between 843 K and 953 K, 1,7-octadiene generates  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ , 1,3-butadiene, 1,4-pentadiene, 1,5-hexadiene, 1-ethyl-1,4-cyclohexadiene, and lower levels of a number of other molecules. The pyrolysis process takes place by a typical radicalic mechanism, mainly with the cleavage of a C–C  $\sigma$  bond. This explains the formation of the smaller molecules from ethene up to pentadiene. Another potential initiation type is the cleavage of a C–H  $\sigma$  bond as shown in the following reaction:



The octadienyl radicals can generate some smaller radicals (frequently by  $\beta$ -scissions) leading to  $\text{C}_2$ ,  $\text{C}_3$ , etc. hydrocarbons. Cyclization reactions are likely to occur [197] generating cyclohexanes, cyclohexenes, cyclopentanes, and cyclopentenes as shown below:

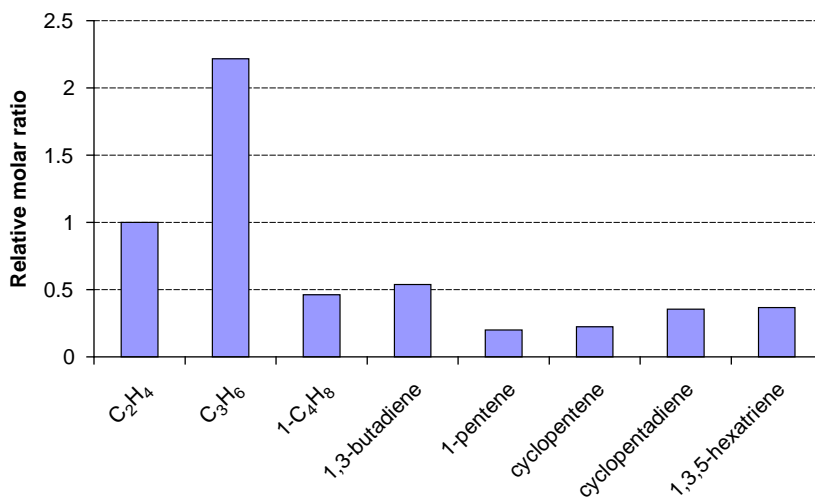
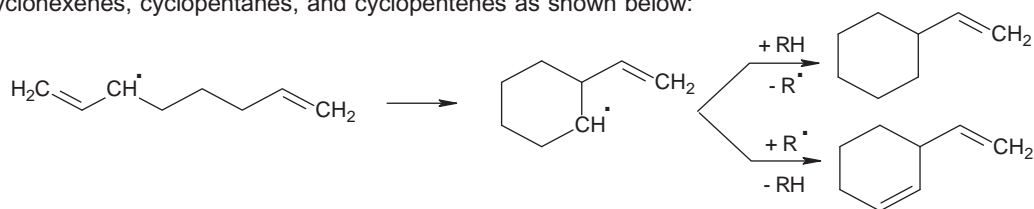
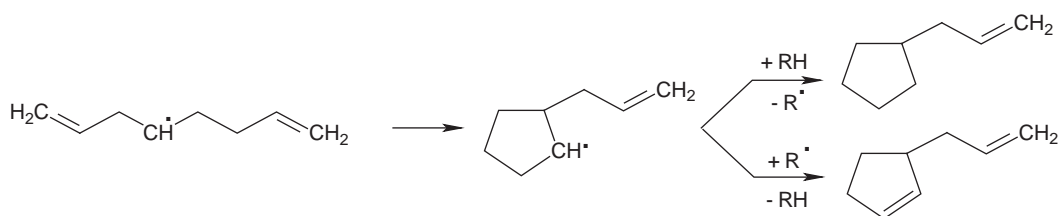


FIGURE 7.4.1. Variation in the mole ratio of pyrolysis products of 1,5-hexadiene at short reaction times.



Further reactions of these cyclic compounds lead to the formation of aromatic hydrocarbons [198].

### Squalene

Squalene ( $C_{30}H_{50}$ ) is an unsaturated hydrocarbon found in animals and some plants and is a precursor of steroids. The IUPAC name of squalene is 2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexaene (MW = 410.7). The compound can be considered a triterpenoid. Results for pyrolysis of a squalene sample are shown in Figure 7.4.2. The pyrolysis was performed on 0.26 mg material using Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280^\circ\text{C}$ . The pyrolysate was analyzed under conditions given in Table 4.6.1. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 7.4.1. The calculation of the mole percent was obtained based solely on peak areas, and since differences in the MS response factors can be quite large, the estimations may have large errors.

As shown in Figure 7.4.2 and Table 7.4.1, squalene pyrolysis generates a large number of compounds. The mechanism of pyrolysis is the same as that for alkenes since the double bonds in this compound are isolated. Fragment molecules, such as 2-methyl-2-butene, 1,3-pentadiene, and 2,7-dimethyl-1,6-octadiene, generated by a  $\beta$ -scission dominate the pyrolysate. Larger fragments of squalene such as (*E,E,E,E*)-2,6,10-trimethylhexadeca-2,6,10,14-tetraene also are detected in the pyrolysate but at low levels. The interesting aspect of squalene pyrolysis is the presence of a relatively large proportion of cyclic and aromatic compounds. 1-Methyl-5-(1-methylethenyl)-cyclohexene and 1-methyl-4-(1-methylethenyl)-cyclohexene (limonene) make-up more than 10% of the pyrolysate.

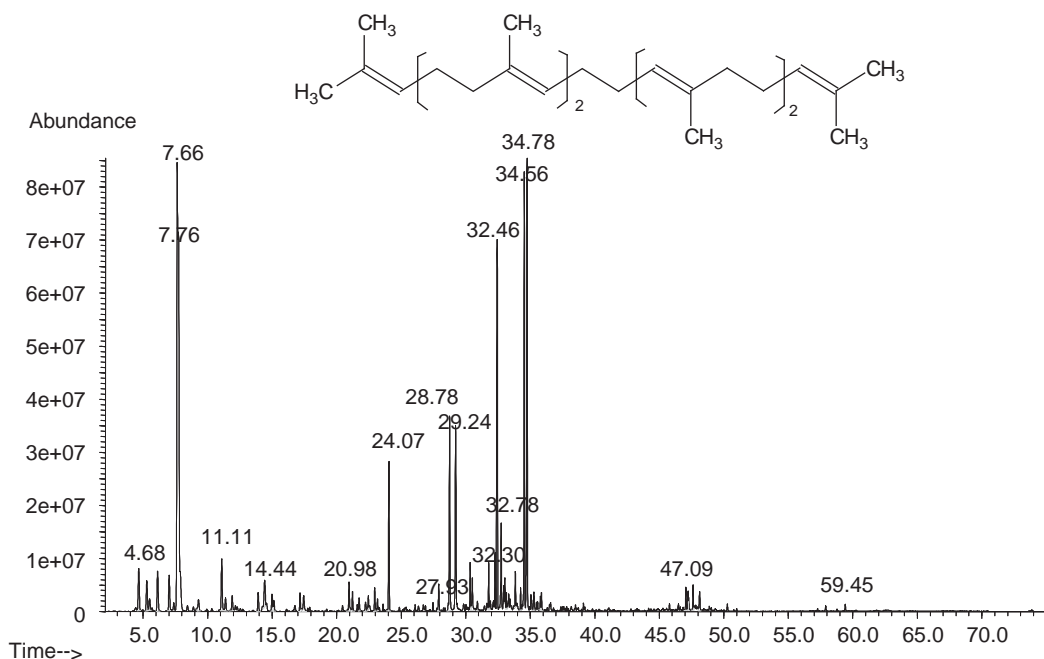


FIGURE 7.4.2. Pyrogram of squalene ( $C_{30}H_{50}$ ) at  $900^\circ\text{C}$ . Peak assignment is given in Table 7.4.1.



TABLE 7.4.1. Identification of the main peaks in the chromatogram shown in Figure 7.4.2 for the pyrolysis of squalene. Hydrogen, methane, and ethylene were not analyzed due to the mass spectrometer settings

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Propene	4.68	42	115-07-1	3.48
2	2-Methyl-1-propene	5.31	56	115-11-7	1.83
3	1,3-Butadiene	5.52	54	106-99-0	0.75
4	3-Methyl-1-butene	6.14	70	563-45-1	1.90
5	2-Methyl-1-butene	7.04	70	563-46-2	1.60
6	2-Methyl-2-butene	7.66	70	513-35-9	20.07
7	1,3-Pentadiene	7.76	68	1574-41-0	18.74
8	4-Methyl-2-pentene	9.31	84	691-38-3	0.49
9	2-Methyl-2-pentene	11.11	84	625-27-4	1.94
10	3-Methyl-2-pentene (Z)	11.40	84	922-62-3	0.49
11	3-Methyl-2-pentene (E)	11.92	84	616-12-6	0.57
12	2,4-Hexadiene (E,E)	13.94	82	5194-51-4	0.68
13	1-Methyl-1,3-cyclopentadiene	14.44	80	96-39-9	1.22
14	5-Methyl-1,3-cyclopentadiene	15.01	80	96-38-8	0.66
15	2,4-Hexadiene (Z,Z)	15.16	82	6108-61-8	0.39
16	2-Methyl-2-hexene	17.18	98	2738-19-4	0.52
17	Benzene	17.47	78	71-43-2	0.72
18	2,5-Dimethyl-2-hexene	20.98	112	3404-78-2	0.72
19	1-Methyl-1,4-cyclohexadiene	21.25	94	4313-57-9	0.48
20	3-Methyl-1,3,5-hexatriene	21.76	94	24587-27-7	0.32
21	2-Methyl-1,3-cyclohexadiene	22.26	94	N/A	0.28
22	2-Methyl-1,3,5-hexatriene	22.48	94	19264-50-7	0.27
23	1,2-Dimethyl-1,3-cyclopentadiene	22.97	94	4784-86-5	0.27
24	1,3-Cycloheptadiene	23.18	94	4054-38-0	0.59
25	Toluene	24.07	92	108-88-3	3.63
26	6-Methyl-5-hepten-1-yne	27.94	108	22842-10-0	0.58
27	2,6-Dimethyl-2,6-octadiene (6Z)	28.78	138	2492-22-0	3.23
28	1,3-Dimethylbenzene ( <i>m</i> -xylene)	29.24	106	108-38-3	4.60
29	2,3,6-Trimethyl-1,5-heptadiene	30.37	138	33501-88-1	0.62
30	1,4-Dimethylbenzene ( <i>p</i> -xylene)	30.54	106	106-42-3	0.79
31	Styrene	30.93	104	100-42-5	0.24
32	4-Ethenyl-1,4-dimethyl-cyclohexene	31.80	136	1743-61-9	0.66
33	2,6-Dimethyl-2- <i>trans</i> -6-octadiene	32.30	138	2609-23-6	0.75
34	2,7-Dimethyl-1,6-octadiene	32.46	138	40195-09-3	7.35
35	3,3,5-Trimethyl-1,5-heptadiene	32.78	138	74630-29-8	1.31
36	1-Methyl-4-(1-methylethylidene)cyclohexene	32.97	136	586-62-9	0.36
37	1-Ethyl-3-methylbenzene	33.05	120	620-14-4	0.49
38	1-Ethyl-2-methylbenzene	33.18	120	611-14-3	0.26
39	1,2,3-Trimethylbenzene	33.35	120	526-73-8	0.30
40	2,6-Dimethyl-2,4,6-octatriene	33.46	136	7216-56-0	0.19

(Continued)

TABLE 7.4.1. *cont'd*

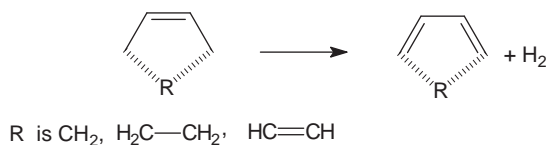
No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
41	1-Cyclohexyl-1-butyne	33.87	136	57497-06-0	0.43
42	1-Methyl-4-(1-methylethyl)-cyclohexene	34.28	138	1195-31-9	0.29
43	1-Methyl-5-(1-methylethenyl)-cyclohexene	34.57	136	13898-73-2	5.99
44	1-Methyl-4-(1-methylethenyl)-cyclohexene (limonene)	34.78	136	138-86-3	6.75
45	1-Ethenyl-4-methylbenzene	35.08	118	622-97-9	0.39
46	3,7-Dimethyl-1,3,6-octatriene	35.31	136	3338-55-4	0.36
47	1,2,4-Trimethylbenzene	35.90	120	95-63-6	0.28
48	( <i>E,E,E</i> )-2,5,10-Trimethyldodeca-2,6,10-triene	47.09	206	N/A	0.23
49	Eudesma-4(1,4),11-diene?	47.25	204	N/A	0.16
50	( <i>Z,E,E</i> )-2,5,10-Trimethyldodeca-2,6,10-triene?	47.31	206	N/A	0.12
51	3,7,7,-Trimethyl-11-methylene-spiro[5,5]undec-2-ene (chamigrene)?	47.65	204	18431-82-8	0.22
52	$\tau$ -Elemene?	48.15	204	30824-67-0	0.25
53	$\beta$ -Elemene?	50.30	204	515-13-9	0.08
54	( <i>E,E,E,E</i> )-2,6,10-Trimethylhexadeca-2,6,10,14-tetraene	57.39	260	N/A	0.05
55	( <i>Z?,E,E,E</i> )-2,6,10-Trimethylhexadeca-2,6,10,14-tetraene	59.45	260	N/A	0.06

Benzene, toluene, and C<sub>2</sub>- and C<sub>3</sub>-alkylbenzenes represent about 5% of pyrolysate. The presence in the pyrolysate of considerably larger amounts of aromatics compared to that found in the pyrolysates of compounds with less unsaturation such as 1-pentadecene or 5-decene (see Section 7.3) shows that a higher unsaturation of the parent compound contributes to a higher yield of aromatics. The formation of PAHs in squalene pyrolysis was not measured, but it is likely that PAHs are formed in squalene pyrolysis.

## 7.5. CYCLOALKENES

### General aspects

Cycloalkenes are hydrocarbons containing a ring of carbon atoms and one or more double bonds in the cycle that do not form an aromatic ring (a cyclic molecule is considered to be aromatic when it follows Hückel's rule, which requires that the number of  $\pi$  electrons equals  $4n+2$  where  $n$  is an integer). Cycloalkene ring systems with one or more double bonds are found in many natural products. Some industrial processes involve cycloalkenes synthesis such as that of cyclohexene, which is typically obtained by catalytic hydrogenation of benzene. Besides practical applications, pyrolysis of cycloolefins has been studied in relation to the formation of aromatic compounds, particularly of those with condensed cycles (PAHs) [199,200]. One of the typical reactions of cycloalkenes with five or six carbon atoms in the cycle is hydrogen elimination by a reaction of the type:



This type of reaction easily forms cyclopentadiene for a five-carbon ring parent compound and benzene for a six-member ring parent compound. Cyclopentadiene also leads to aromatic compounds when further heated. Ring substitution does not affect adversely the formation of aromatic compounds.

### Cyclopropene, cyclobutene, and cyclobutadiene

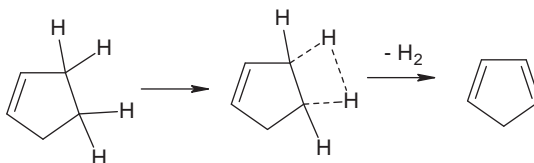
Cyclopropene is the smallest cycloalkane with a highly strained ring. When heated at about 425 °C, cyclopropene isomerizes to methylacetylene. The ring of cyclopropene is present in certain naturally occurring compounds such as malvalic acid and sterculic acid.

Cyclobutene (C<sub>4</sub>H<sub>6</sub>) has a high strained ring and suffers isomerization upon heating [201]. Various organic syntheses are based on this ring opening during heating [202].

Cyclobutadiene is an extremely unstable compound (5-s lifetime in free state at low temperatures). At temperatures as low as 35 K, cyclobutadiene forms a dimer. Some complexes of cyclobutadiene involving its  $\pi$  electron system are more stable. Examples of such molecules are Fe(C<sub>4</sub>H<sub>4</sub>)(CO)<sub>3</sub> and Ru(C<sub>4</sub>H<sub>4</sub>)(CO)<sub>3</sub>.

### Cyclopentene

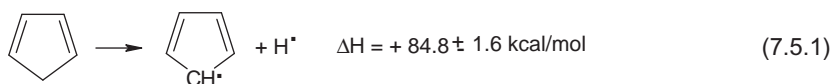
Cyclopentene decomposes upon heating starting at temperatures around 600 °C with the formation of cyclopentadiene [203,204]. The reaction has a unimolecular mechanism and can be written as follows:



Typical for a unimolecular reaction, the rate varies with the gas pressure, and a limiting high-pressure rate constant  $k^\infty$  as well as a falloff pressure  $P_{1/2}$  can be determined. For temperatures between 505 °C and 510 °C, a  $k^\infty$  of about  $3.55 \times 10^{-4} \text{ s}^{-1}$  was measured [205]. Other kinetic parameters also were measured at very low pressure and temperature range 942 K to 1152 K [206].

### Cyclopentadiene and methylcyclopentadiene

Cyclopentadiene pyrolysis is a process studied extensively due to the potential role as an intermediate molecule in the generation of PAHs during the pyrolysis of many other organic compounds [207–213]. The initiation reaction for cyclopentadiene pyrolysis starting around 600 °C is the formation of cyclopentadienyl radical as follows:

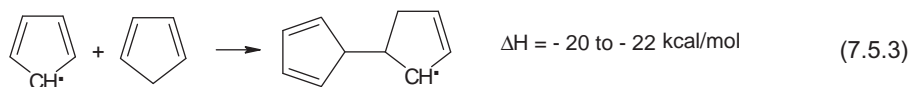


$\Delta H$  of formation for cyclopentadiene (gas) is  $32.1 \pm 0.4 \text{ kcal/mol}$  and for cyclopentadienyl radical is  $64.7 \pm 1.9 \text{ kcal/mol}$  [214]. The rate constant for this reaction is described by Arrhenius equation:

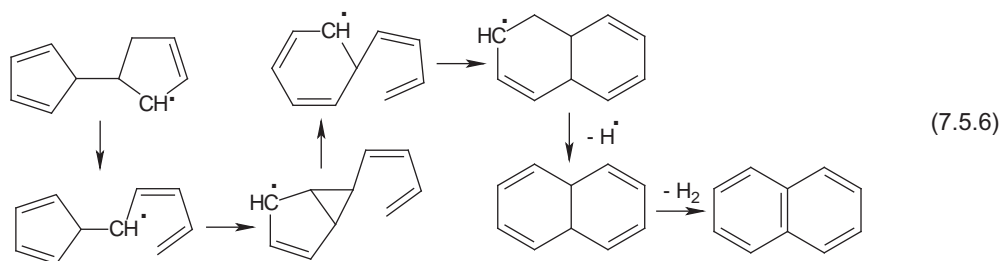
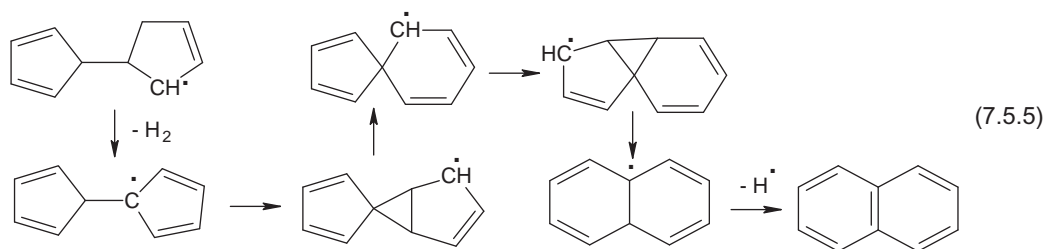
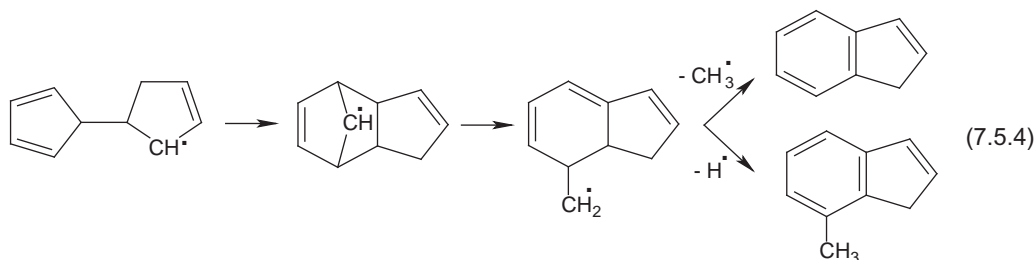
$$k = 2.5 \times 10^{15} \exp\left(\frac{-82000(\text{cal/mol})}{RT}\right) \text{ cm}^3/\text{mol/s} \quad (7.5.2)$$

Pentadienyl radical can react easily with a second cyclopentadiene molecule (energy barrier for this formation is 11.5 kcal/mol) to produce a dimer radical (C<sub>5</sub>H<sub>5</sub>–C<sub>5</sub>H<sub>6</sub>•) that is stabilized by resonance.

The reaction is shown below:

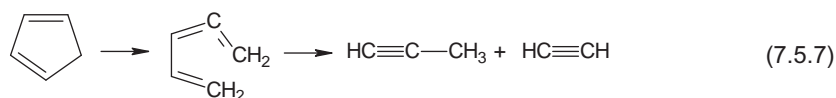


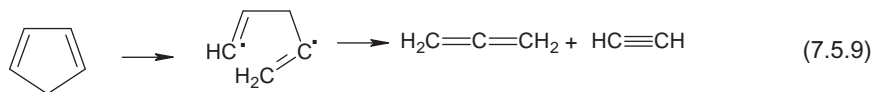
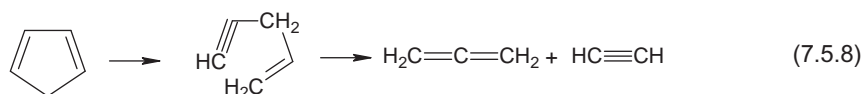
This dimer radical continues a chain of reactions, with the formation of indene, 7-methylindene, and naphthalene. The probable paths of these reactions can be written as follows:



Both indene and naphthalene upon further heating can generate heavier PAHs. As an example, the chain of reactions 7.1.48 shows the transformation of naphthalene into benzo[*k*]fluoranthene.

Other reactions are possible during cyclopentadiene thermal degradation. Three such reactions leading to very reactive compounds are indicated below:





The interaction of the reactive compounds generated in reactions 7.5.7–7.5.9 contributes further to the formation of compounds such as benzene, fulvene, naphthalene, azulene, and heavier aromatic compounds.

Some kinetic parameters of the reactions considered for pyrolysis of cyclopentadiene were evaluated by experimental and theoretical procedures [213,215,216], some of them are indicated in Table 7.5.1 together with the parameters in Arrhenius equation.

Besides the mechanisms previously indicated, other potential routes were proposed for explaining the formation of PAHs in pyrolysis and combustion of cyclic  $\text{C}_5$  species. One such route involves the formation of 9-H-fulvalenyl radical ( $\text{C}_5\text{H}_5\text{--C}_5\text{H}_4^\bullet$ ) generated, for example, from the cyclopentadienyl radical and cyclopentene with hydrogen elimination. The formation of this radical explains the formation during pyrolysis of fulvalene and of PAHs containing  $\text{C}_5$  cycles that are possible fullerene precursors [216].

1-Methylcyclopentadiene and 2-methylcyclopentadiene are practically stable below  $500^\circ\text{C}$ , and only a low level of about 5% of a mixture of other isomers (e.g., 5-methylcyclopentadiene) is formed. At  $680^\circ\text{C}$ , 95% of the compound is decomposed, with the formation of benzene and cyclopentadiene as the main pyrolysis products. Some lower molecular weight compounds as well as toluene and heavier compounds are generated at lower levels. At temperatures around  $800^\circ\text{C}$ , the level of generated benzene remains about the same while the formation of cyclopentadiene decreases. Cyclopentadiene is formed by the cleavage of the C–C bond between the cycle and the methyl radical. The reaction of benzene formation can take place following the mechanism shown below:

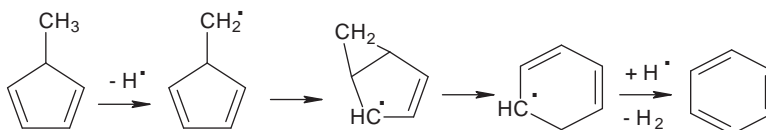
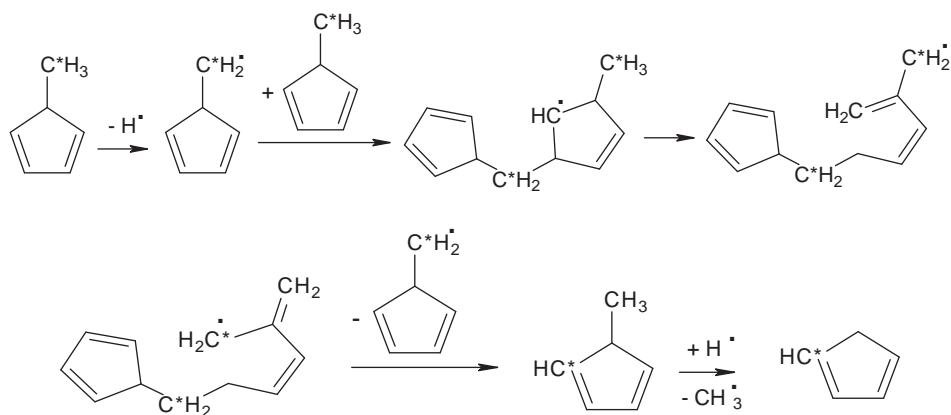


TABLE 7.5.1. Reactions involved in cyclopentadiene pyrolysis and some kinetic parameters of these reactions [216]

Reaction	$A$ ( $\text{mol cm}^3 \text{ s}$ )	$E^\ddagger$ (cal)
$\text{Cyc-C}_5\text{H}_6 \rightarrow \text{CH}_2=\text{CH-CH}=\text{C}=\text{CH}_2$	$1.35 \times 10^{15}$	80,450
$\text{CH}_2=\text{CH-CH}=\text{C}=\text{CH}_2 \rightarrow \text{CH}\equiv\text{C-CH}_3+\text{C}_2\text{H}_2$	$2.88 \times 10^{13}$	66,550
$\text{Cyc-C}_5\text{H}_6+\text{H}^\bullet \rightarrow \text{Cyc-C}_5\text{H}_5^\bullet+\text{H}_2$	$3.00 \times 10^{14}$	6640
$\text{Cyc-C}_5\text{H}_6 \rightarrow \text{C}_2\text{H}_2+\text{CH}_2=\text{C}=\text{CH}_2$	$3.80 \times 10^{17}$	104,000
$\text{Cyc-C}_5\text{H}_6 \rightarrow \text{CH}_2=\text{CH-CH}_2\text{-C}\equiv\text{CH}$	$8.5 \times 10^{14}$	90,540
$\text{CH}_2=\text{CH-CH}_2\text{-C}\equiv\text{CH} \rightarrow \text{C}_2\text{H}_2+\text{CH}_2=\text{C}=\text{CH}_2$	$3.55 \times 10^{13}$	63,360
$\text{Cyc-C}_5\text{H}_6+\text{CH}_2=\text{CH}^\bullet \rightarrow \text{Cyc-C}_5\text{H}_5^\bullet+\text{C}_2\text{H}_4$	$6.00 \times 10^{12}$	0
$\text{Cyc-C}_5\text{H}_6+\text{CH}\equiv\text{C-CH}_2^\bullet \rightarrow \text{Cyc-C}_5\text{H}_5^\bullet+\text{CH}\equiv\text{C-CH}_3$	$1.10 \times 10^{11}$	5500
$\text{Cyc-C}_5\text{H}_6+\text{Cyc-C}_6\text{H}_5^\bullet \rightarrow \text{Cyc-C}_5\text{H}_5^\bullet+\text{Cyc-C}_6\text{H}_6$	$3.10 \times 10^{11}$	5500
$\text{Cyc-C}_5\text{H}_6+\text{CH}_3^\bullet \rightarrow \text{Cyc-C}_5\text{H}_5^\bullet+\text{CH}_4$	$5.00 \times 10^{11}$	5500
$\text{Cyc-C}_5\text{H}_6+\text{CH}_2=\text{CH-CH}_2^\bullet \rightarrow \text{Cyc-C}_5\text{H}_5^\bullet+\text{C}_3\text{H}_6$	$1.10 \times 10^{11}$	5500
$\text{Cyc-C}_5\text{H}_6+\text{Cyc-C}_5\text{H}_6 \rightarrow \text{Naphthalene}+2\text{H}^\bullet$	$2.00 \times 10^{13}$	8000

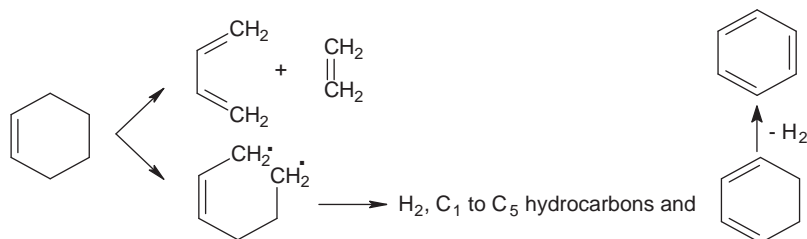
Formation of benzene through a fulvenyl radical is possible as well. The opening of the cyclopentadiene ring is another potential route for benzene formation. This mechanism is supported by the formation of a certain percentage of  $^{14}\text{C}$ -labeled cyclopentadiene during the pyrolysis of [methyl- $^{14}\text{C}$ ]methylcyclopentadiene [199]. This potential route of decomposition is indicated below (\* indicates labeled carbon):



Other reaction paths for cyclopentadienes pyrolysis have been investigated and are reported in the literature [217].

### Cyclohexene, cyclohexadiene, and their alkyl substituted homologs

Pyrolysis of cyclohexene starting between 425 °C and 535 °C leads to various fragment molecules including ethylene, butadiene, cyclohexadiene, and a number of molecules containing between one and five carbon atoms. Benzene and methylcyclopentane are also present in the pyrolysate. Two main mechanisms are probably involved in cyclohexene decomposition, one being a retro-Diels–Alder reaction and the other the formation of the cyclohexenyl biradical, as shown below:



The overall consumption of cyclohexene has a first order kinetics with the rate constant given by [128]:

$$k = 10^{15.89} \exp\left(\frac{-283000 \text{ (J/mol)}}{RT}\right) \text{ s}^{-1} \quad (7.5.10)$$

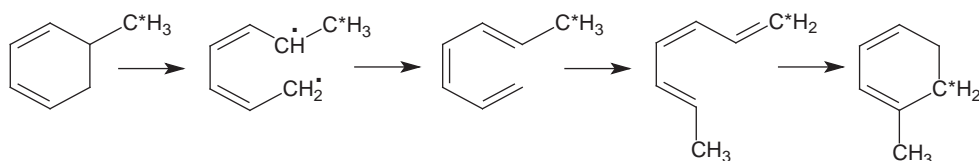
Some other studies attempted to evaluate which of the two reactions is dominant. The excess of butadiene and ethylene in the initial phases of thermal decomposition of cyclohexene in the range of temperatures 541–629 °C indicated that retro-Diels–Alder is very likely the main reaction path [218]. Rate constants for the generation of various products are reported in the literature [219].

Two cyclohexadienes with the double bonds in the positions 1,3 and 1,4 are known. The main pyrolysis product of both compounds is benzene with small quantities of lighter compounds ( $\text{C}_n$ ,  $n < 5$ ) and heavier aromatics. However, 1,4-cyclohexadiene eliminates hydrogen more easily than

1,3-cyclohexadiene upon heating. The heats of formation of the two isomers of cyclopentadiene are about the same ( $25.4 \pm 0.4$  kcal/mol for 1,3-isomer and  $24.9 \pm 0.6$  kcal/mol for 1,4-isomer), and the dehydrogenation reaction with the formation of benzene is exothermic for both isomers.

A detailed study by homogeneous gas-phase pyrolysis of 1,4-cyclohexadiene proved that the reaction obeys the pattern of reactivity of cyclic olefins. The process is of first order until at least 80% of the initial compound is decomposed. The rate constant at temperatures between 330 °C and 390 °C and pressures between  $10^{-3}$  Torr and  $10^2$  Torr has the expression  $\log k = (12.36 \pm 0.13) - (43.8 \pm 0.4 \text{ kcal/mol}) / (2.303 RT)$ . The reaction mechanism does not involve the formation of hydrogen atoms, as shown by the lack of isotopic exchange with hexadeuterobenzene and toluene. The chain decomposition involving the formation of cyclohexadienyl radicals is, therefore, not important, probably due to the endothermicity and low *A*-factor of the bimolecular initiation [220].

The study of pyrolysis mechanism of alkyl cyclohexadienes was performed particularly on [methyl- $^{14}\text{C}$ ]methyl-1,3-cyclohexadiene(s) and [methyl- $^{14}\text{C}$ ]1-methyl-1,4-cyclohexadiene [199]. [Methyl- $^{14}\text{C}$ ]methyl-1,3-cyclohexadiene(s) suffer considerable isomerization around 500 °C, but only a low proportion of dehydrogenation. At temperatures higher than 650 °C, the main liquid pyrolysis products are benzene and toluene with small amounts (less than 5%) of higher molecular weight aromatics (gaseous smaller molecules are also generated). At temperatures higher than 750 °C, toluene starts a demethylation process (at 750 °C, pure toluene is about 12% demethylated). When the pyrolysis started with [methyl- $^{14}\text{C}$ ]methyl-1,3-cyclohexadiene(s), all aromatics were found to be labeled [199]. Toluene was labeled both at the methyl group and, to a considerable extent, in the ring. The proportion of ring-labeled toluene increased continuously when temperature increased from 600 °C to 750 °C. The presence of the labeled carbon in the aromatic ring of the pyrolysis products of 1,3-cyclohexadiene indicates that, among other reactions, a cycle opening takes place, as shown below:



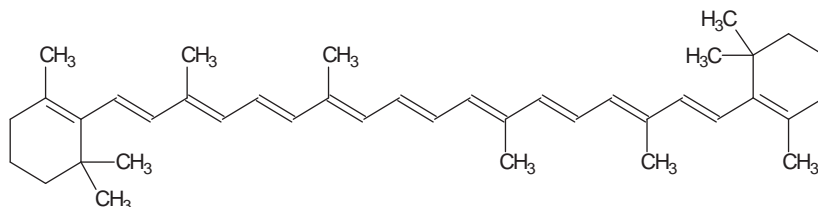
[Methyl- $^{14}\text{C}$ ]1-methyl-1,4-cyclohexadiene undergoes a dehydrogenation to toluene even at temperatures below 500 °C. This reaction takes place by a 1,4-hydrogen elimination (symmetry allowed). Besides toluene, another product in the pyrolysate is methylcyclohexane, which is present at a lower level (less than 10%). This compound is probably formed by disproportionation. At temperatures higher than 600 °C, the compounds present in the pyrolysate include mainly toluene and lower levels of benzene plus some nonaromatic degradation products. The percentage of  $^{14}\text{C}$ -labeled toluene in the ring is very small even at high temperatures ( $1.0 \pm 0.5\%$  at 780 °C). The 1,4-dehydrogenation reaction is probably considerably faster than any ring opening reactions.

The study of the inclusion of a labeled carbon in the ring of a  $\text{C}_6$  cyclic hydrocarbon during pyrolysis also has been studied for [7- $^{14}\text{C}$ ]methylenecyclohexane. This compound forms upon heating, before decomposition and aromatization, a mixture of isomers including the compound itself, 1-methylcyclohexene and possibly 3-methylcyclohexene. At 700 °C, the mixture of isomers is converted into toluene (22 wt.%), benzene (18 wt.%), and gaseous products with less than five carbon atoms (60 wt.%). The content of  $^{14}\text{C}$  label in the ring of toluene was found to be  $45 \pm 4\%$  [199].

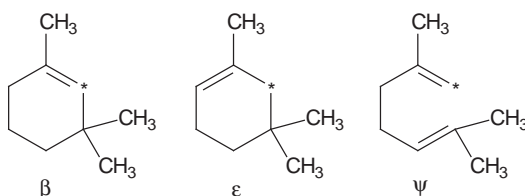
## Carotene

Carotenes are polyenes with the ends consisting of either one or two unsaturated cycles. They are considered tetraterpenes, having the general formula  $\text{C}_{40}\text{H}_{56}$ . Carotenes are present in plants and are related to several other compounds of biological importance such as retinal and vitamin A (retinol). The most common carotenes are  $\alpha$ -carotene and  $\beta$ -carotene, and besides these,  $\gamma$ -,  $\delta$ -,  $\epsilon$ -, and  $\zeta$ -carotene

are known. The structure of  $\beta$ -carotene is shown below:



A specific nomenclature aims to describe the two ends of the carotene molecule. The end may consist of a  $\beta$ -ring, an  $\epsilon$ -ring, or can be an uncyclized end labeled as  $\psi$ . In this nomenclature  $\beta$ -carotene is indicated as  $\beta,\beta$ -carotene,  $\alpha$ -carotene as  $\beta,\epsilon$ -carotene, and  $\gamma$ -carotene as  $\beta,\psi$ -carotene. Results for pyrolysis of a  $\beta$ -carotene sample are shown in Figure 7.5.1. The pyrolysis was performed on 0.26 mg material using Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280^\circ\text{C}$ . The pyrolysate was analyzed under conditions given in Table 4.6.1. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 7.5.2. The calculation of the mole percent was obtained based solely on peak areas, and since differences in the MS response factors can be quite large, the estimations may have large errors.



Since the only procedure used for peak identification in the pyrogram shown in Figure 7.5.1 is a mass spectral library search, the accuracy of the results is limited to the correctness of the match. For example, various structures are possible for the peak eluting at 46.95 min. This peak was assigned as 1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene (structure 1 in Figure 7.5.2), although compounds 2, 3, and 4 have a very similar spectrum.

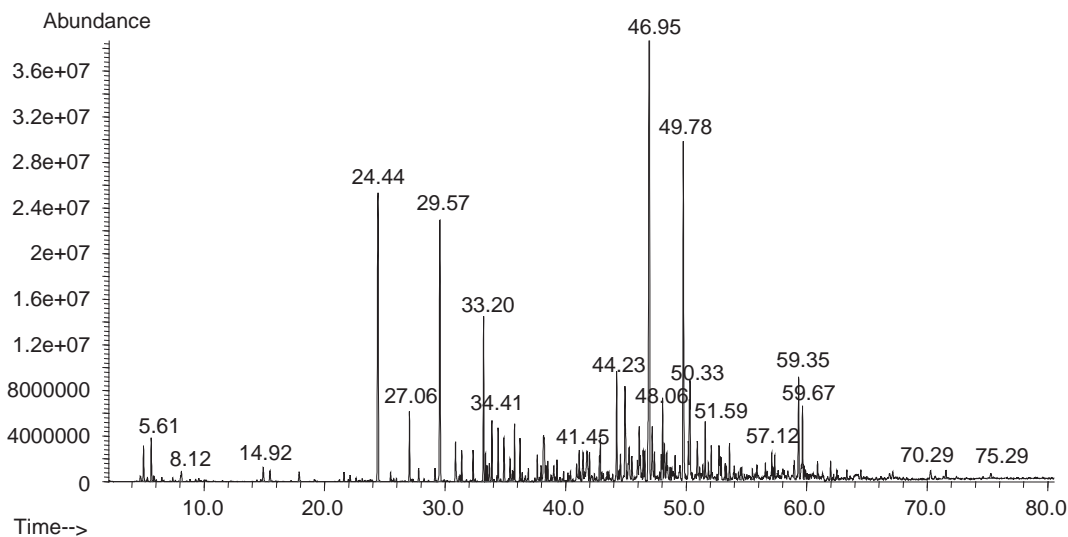


FIGURE 7.5.1. Pyrogram of  $\beta,\beta$ -carotene ( $\text{C}_{40}\text{H}_{56}$ ) at  $900^\circ\text{C}$ . Peak assignment is given in Table 7.5.2.



TABLE 7.5.2. Identification of the main peaks in the chromatogram shown in Figure 7.5.1 for the pyrolysis of  $\beta,\beta$ -carotene (hydrogen, methane, and ethylene were not analyzed due to the mass spectrometer settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Propene	4.97	42	115-07-1	2.58
2	2-Methyl-1-propene	5.61	56	115-11-7	2.27
3	2-Methyl-1,3-butadiene (isoprene)	8.12	68	78-79-5	0.70
4	1-Methyl-1,3-cyclopentadiene	14.92	80	96-39-9	0.69
5	1,3-Cyclohexadiene	15.48	80	592-57-4	0.49
6	Benzene	17.90	78	71-43-2	0.47
7	Toluene	24.44	92	108-88-3	12.52
8	1,2,4,4-Tetramethylcyclopentene	27.06	124	65378-76-9	1.52
9	1,5-Dimethyl-1,4-cyclohexadiene	27.82	108	4190-06-1	0.32
10	Ethylbenzene	29.17	106	100-41-4	0.44
11	1,3-Dimethylbenzene ( <i>m</i> -xylene)	29.57	106	108-38-3	9.39
12	1,4-Dimethylbenzene ( <i>p</i> -xylene)	30.87	106	106-42-3	1.29
13	1-Methyl-3-(1-methylethenyl)cyclohexene	31.39	136	499-03-6	0.57
14	2-(2-isopropylidene-3-methylcyclopropyl)-propane?	32.33	138	24524-51-4	0.58
15	1,2,3,4,5-Pentamethylcyclopentene	33.20	138	N/A	3.23
16	1-Ethyl-3-methylbenzene	33.36	120	620-14-4	0.56
17	1-Ethyl-4-methylbenzene	33.49	120	622-96-8	0.32
18	1,2,5,5-Tetramethyl-1,3-cyclopentadiene	33.68	122	4249-12-1	0.50
19	2,6,6-Trimethyl-1-methylenecyclohex-2-ene	33.89	136	514-95-4	1.17
20	3,3-Dimethyl-6-methylene-1-cyclohexene	34.41	122	20185-16-4	1.14
21	1,3,5-Trimethylbenzene	34.89	120	108-67-8	0.59
22	2,2,8-Trimethylbicyclo(4,2,0)oct-1-ene	34.91	150	60714-22-9	0.53
23	2-Propenylbenzene	35.40	118	300-57-2	0.49
24	1-Propenylbenzene	35.59	118	637-50-3	0.19
25	2-Ethenyl-1,3,3-trimethylcyclohexene	35.77	150	5293-90-3	0.91
26	1,2,4-Trimethylbenzene	36.22	120	95-63-6	0.84
27	Unknown	37.65	150	N/A	0.46
28	1H-indene	37.96	116	95-13-6	0.34
29	1-Ethyl-3-(1-methylethyl)benzene	38.18	148	4920-99-4	2.15
30	1,3,5,5,6,6,-Hexamethyl-1,3-cyclohexadiene?	38.38	164	N/A	0.25
31	1-Methyl-2-(2-propenyl)benzene	38.53	132	1587-04-8	0.41
32	1-Ethyl-4-(1-methylethyl)benzene	39.02	148	4218-48-8	0.40
33	1,3-Dimethyl-5-(1-methylethyl)benzene	39.29	148	4706-90-5	0.36
34	2,3-Dihydro-5-methyl-1H-indene	40.92	132	874-35-1	0.48
35	1-(1,1,3-Trimethyl-2-butenyl)-1-cyclohexene	41.13	178	116996-62-4	0.41
36	3-Methyl-1H-indene	41.45	130	767-60-2	0.81
37		41.78	162	N/A	1.28

(Continued)

TABLE 7.5.2. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
	1-(Prop-1-enyl)-2,6,6-trimethylcyclohexadiene or isomer				
38	2-(1-Butenyl)-1,3,3-trimethylcyclohex-1-ene	41.99	178	N/A	0.42
39	4-Ethyl-1-ethenylbenzene+MW = 178	42.81	132	354-07-7	0.47
40	3-Methyl-1-(2,6,6-trimethylcyclohex-1-enyl)buta-1,3-diene	42.88	190	N/A	0.55
41	1,1,4-Trimethyl-2,3-dihydro-1H-indene	44.23	160	16204-72-1	1.91
42	1,1-Dimethyl-1H-indene	44.55	144	18636-55-0	0.66
43	3-Methyl-1-(2,6,6-trimethylcyclohex-1-enyl)buta-1,3-diene isomer	44.93	190	N/A	2.05
44	4,7-Dimethylindene	45.50	144	6974-97-6	0.56
45	1,2,3-Trimethyl-1H-indene	46.11	158	4773-83-5	0.94
46	3-Methyl-1-(2,6,6-trimethylcyclohex-1-enyl)penta-1,3-diene isomer	46.43	204	N/A	0.50
47	1,1,6-Trimethyl-1,2,3,4-tetrahydronaphthalene isomer	46.57	174	N/A	0.48
48	1,1,6-Trimethyl-1,2,3,4-tetrahydronaphthalene	46.95	174	475-03-6	15.97
49	1,2-Dihydro-1,1,6-trimethylnaphthalene	47.20	172	30364-38-6	1.21
50	1-Methylnaphthalene	47.39	142	90-12-0	0.57
51	Unknown	47.94	188	N/A	0.47
52	1,1,3-Trimethyl-1H-indene	48.06	158	2177-45-9	1.50
53	1,2,3-Trimethyl-1H-indene	48.21	158	4773-83-5	0.81
54	(1-Methylpenta-2,4-dienyl)benzene	48.40	158	N/A	0.51
55	1,2,3,4-Tetrahydro-5,6,7,8-tetramethylnaphthalene	49.10	188	19063-11-7	0.35
56	2,6-Dimethylnaphthalene	49.78	156	581-42-0	7.69
57	1,3-Dimethylnaphthalene	50.19	156	575-41-7	0.66
58	1,2,3,4,5,6,7,8-Octahydro-9,10-dimethylantracene	50.28	214	42173-25-1	0.82
59	1,7-Dimethylnaphthalene	50.33	156	575-37-1	1.79
60	Unknown	50.94	216	N/A	0.70
61	2-(2-Methylpenta-1,3-dienyl)-7,7-dimethyl-3,4,5,6,7-pentahydroindene	51.59	228	N/A	0.70
62	Unknown	52.10	228	N/A	0.31
63	1,6,7-Trimethylnaphthalene	52.74	170	2245-38-7	0.57
64	1,2,3,4,5,6,7,8-Octahydro-1-methylantracene	52.81	200	N/A	0.27
65	2,3,6-Trimethylnaphthalene	52.92	170	829-26-5	0.36
66	1-Methyl-3-[(4-methylphenyl)methyl]benzene	53.25	196	21895-16-9	0.17
67	1,4,6-Trimethylnaphthalene	53.35	170	2131-42-2	0.23
68	4,6,8-Trimethylazulene	53.61	170	941-81-1	0.55
69	Unknown	54.00	182	N/A	0.31
70	1,6-Dimethyl-4-(1-methylethyl)naphthalene	54.63	198	483-78-3	0.21
71	Unknown	56.59	240	N/A	0.21

(Continued)

TABLE 7.5.2. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
72	Carotene fragment	59.35	240	N/A	1.25
73	Carotene fragment	59.67	240	N/A	0.84
74	Carotene fragment	60.92	240	N/A	0.17
75	Unknown	63.36	268	N/A	0.09
76	2,3,5-Trimethylphenanthrene	70.29	220	3674-73-5	0.19
77	Carotene fragment	71.57	292	N/A	0.13
78	3,4,5,6-Tetramethylphenanthrene	75.29	234	7343-06-8	0.16

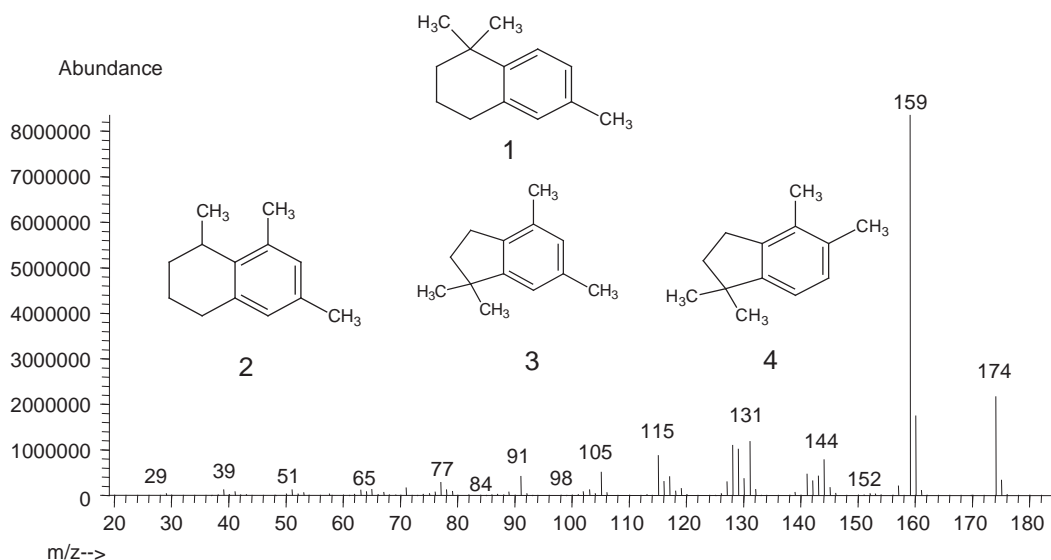
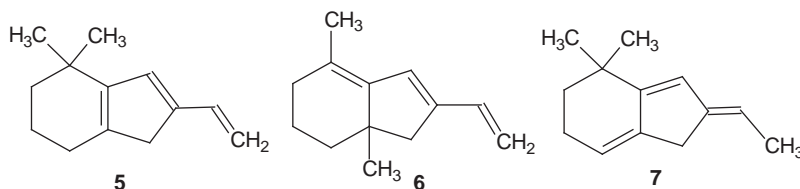


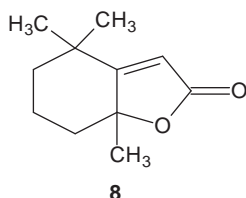
FIGURE 7.5.2. Spectrum of the peak eluting at 46.95 min in the pyrogram of  $\beta,\beta$ -carotene and assigned to 1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene (structure 1) and other possible compounds (structures 2, 3, and 4) with very similar spectra.

At the same time, other possible compounds able to generate the peak eluting at 46.95 min in the pyrogram of  $\beta,\beta$ -carotene, such as 7,7-dimethyl-2-vinyl-3,4,5,6,7-pentahydroindene (structure 5), 7,3a-dimethyl-2-vinyl-3,4,5,6,3a-pentahydroindene (structure 6), or 2-ethylidene-7,7-dimethyl-3,5,6,7-tetrahydroindene (structure 7) are not present in current mass spectral libraries and are not listed as possible compounds to generate the spectrum shown in Figure 7.5.2.



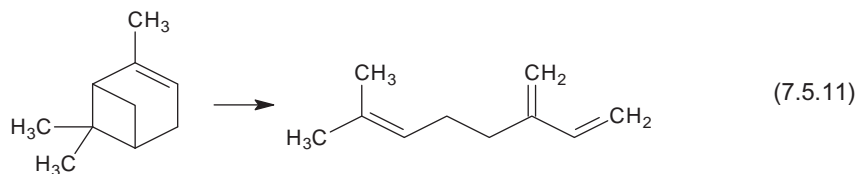
The identification of heavier compounds becomes less certain as the molecular weight of the fragment molecule increases. However, the formation of cyclic aromatic compounds such as derivatives of indene, naphthalene, anthracene, and phenanthrene are a clear indication that PAHs can be formed easily by the pyrolysis of carotene and related compounds. The PAHs were not specifically analyzed in the pyrolysate, and the levels of other PAHs potentially present in the pyrolysate are likely to be below

the sensitivity of a direct GC/MS analysis. Carotene itself is easily oxidized in air. Pyrolysis products of the oxidized material generates numerous oxygen containing compounds, the main one in the pyrolysate of oxidized carotene being 5,6,7,7a-tetrahydro-4,4,7a-trimethyl-2(4H)-benzofuranone (structure **8**). A study regarding the correlation between the formation of PAHs and the structure of the parent compound from other terpenes during pyrolysis has been reported in the literature [221].



### Other cycloalkenes

Thermal decomposition of cycloalkenes is a complex process, and a variety of reactions may take place upon heating such that more stable molecules are formed from the parent molecule. One such example is the transformation of  $\alpha$ -pinene in myrcene [221]. The reaction takes place as follows:



The reaction is used for the preparation of myrcene, which is used as an intermediate for other syntheses.

## 7.6. ALKYNES

### General aspects

Alkynes contain in their molecule a triple bond between two carbon atoms. The triple bond is formed from a  $\sigma$  bond (between the  $sp$  orbitals of the two carbons with  $sp$  hybridization) and two  $\pi$  bonds between the  $p_y$  and  $p_z$  orbitals of the two carbon atoms. The triple bond is very stable to thermal decomposition. For example, in acetylene the  $C\equiv C$  bond strength is  $230.6 \pm 0.7$  kcal/mol [133] (see Table 3.1.1).

The most important compound of this class is acetylene ( $C_2H_2$ ), which has a large number of industrial applications and is obtained mainly by a pyrolytic process from ethylene and from various oil fractions. Acetylene also is obtained from  $CaC_2$  by hydrolysis. Vinylacetylene ( $CH\equiv C-CH=CH_2$ ) has some industrial importance (used in the past in chloroprene production).

### Acetylene

Pyrolysis of acetylene is the subject of various studies [222–230]. The interest in this process is related mainly to the finding that the generation of PAHs in the flame of various hydrocarbons involves acetylene as a precursor. Pyrolyzed between 854 K and 970 K, acetylene generates the dimer vinylacetylene (1-buten-3-yne) and low levels of benzene with conversion between 0.0022% and 1.4%. The decomposition starts above 673 K, but at this temperature only low traces of the two compounds can be detected. At 68 Torr and 936 K in a flow system using a 2 mm-i.d. heated quartz tube, the formation of vinylacetylene and benzene as a function of residence time in the reactor is shown in Figure 7.6.1 [222].

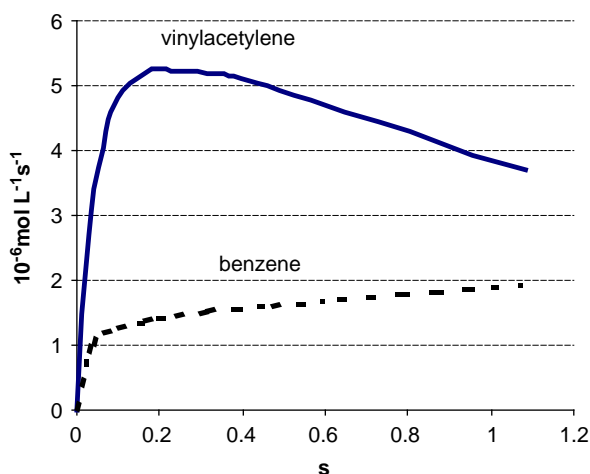


FIGURE 7.6.1. Formation of vinylacetylene and benzene from acetylene, in a flow system at 936 K and 68 Torr [222].

The mechanism of vinylacetylene formation has been debated in a number of papers [228,230–232]. One such mechanism assumes the formation of vinylidene ( $\text{CH}_2=\text{C}:$ ) followed by the reaction of two such molecules to generate vinylacetylene [233]. Another mechanism assumed a disproportionation reaction with the formation of  $\text{C}_2\text{H}^\bullet$  and  $\text{C}_2\text{H}_3^\bullet$  free radicals [230]. The most probable initiation reaction that dominates acetylene decomposition around 900 K is the following:



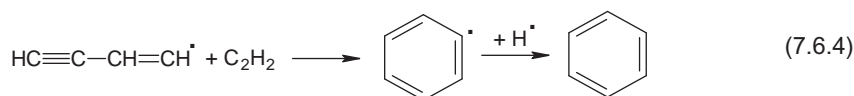
The termination following the initiation shown in reaction 7.6.1 is very likely a bimolecular reaction of the type:



The kinetic parameters for the formation of vinylacetylene were measured in several studies [222,232,234]. One of these studies [222] showed that the steady-state formation of vinylacetylene reaction rate order is 1.8 and the rate constant is given by the expression:

$$k = 10^{22.7 \pm 1.5} \exp\left(\frac{-165 \pm 11(\text{kJ})}{RT}\right) \text{ L/mol/s} \quad (7.6.3)$$

The formation of benzene from acetylene should be overall an exothermic reaction ( $\Delta H_f^\circ = +54.54$  kcal/mol for acetylene and  $\Delta H_f^\circ = +19.8$  kcal/mol for benzene). Considering the entropic factor, however ( $\Delta S_f^\circ = +47.98$  cal/T/mol for acetylene and  $\Delta S_f^\circ = +64.36$  cal/T/mol for benzene), the increase in temperature does not favor the formation of benzene in a trimolecular reaction. High reaction barriers also are likely to make this reaction not favored [235]. The mechanism of benzene formation is probably a result of further reaction of the radical  $\text{C}_4\text{H}_3^\bullet$  with a molecule of acetylene followed by a termination reaction with a hydrogen atom.



The steady-state formation of benzene reaction rate order is 2.4, and the rate constant is given by the expression:

$$k = 10^{15.6 \pm 1.1} \exp\left(\frac{-100 \pm 9(\text{kJ})}{RT}\right) \text{L}^{1.4}/\text{mol}^{1.4}/\text{s} \quad (7.6.5)$$

At temperatures above 900 °C (1173 K), the initiation reaction that plays an important role in acetylene decomposition is the cleavage of a C–H bond ( $\Delta H = +133.0 \text{ kcal/mol}$ ):

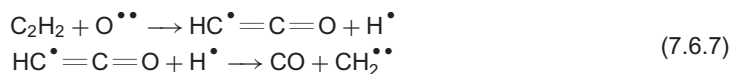


Kinetic parameters for this reaction have been reported in the literature [229]. The reaction products include (besides vinylacetylene and benzene) diacetylene ( $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$ ), triacetylene ( $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{CH}$ ), and even tetraacetylene. The main product at long heating times and high temperature is soot (carbon black composed mainly of amorphous carbon with some low content of hydrogen). Diacetylene, triacetylene, etc. are probably generated by more than one mechanism, including decomposition of vinylacetylene and reactions of the free radicals.

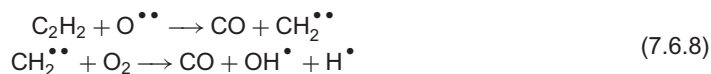
Acetylene pyrolysis was studied also for heterogeneous decomposition (on a hot carbon film) [236], vacuum carburizing of steel [237], production of nanotubes [238], pyrolysis in the presence of acetone (at 0.1% or higher), and pyrolysis in the presence of neopentane [239].

Acetylene combustion with oxygen produces a flame of over 3300 °C (6000 °F), releasing 11.8 kJ/g as a result of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  formation. At lower oxygen concentration, CO and  $\text{H}_2\text{O}$  are the main combustion products. Oxyacetylene is the hottest burning common fuel gas ( $\text{C}_2\text{N}_2$  burning produces an even higher temperature). The oxyacetylene flame can have a stoichiometric composition, an excess of oxygen, or an excess of acetylene. The flame burning with an excess of acetylene produces a considerable amount of soot (incomplete burning). Besides carbon, this soot contains various levels of PAHs. Much effort has been invested in the research of the formation of soot and PAHs in acetylene flames [154,240–243]. Since pyrolysis of several other hydrocarbons also leads to the formation of acetylene, the study of acetylene burning is considered a key in the understanding of PAH formation during the burning of carbonaceous compounds (particularly hydrocarbons).

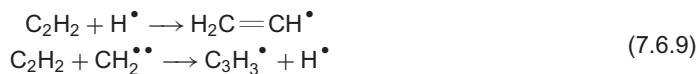
PAHs are basically formed in acetylene flame through pyrolytic processes. The parallel combustion process influences the pyrolysis by generating more free radicals (and of different species), particularly through the formation of more hydrogen atoms and  $\text{OH}^\bullet$  and  $\text{OOH}^\bullet$  free radicals. Also, the presence of oxygen plays a role in termination reactions, removing some of the free radicals. The process is, however, very complex, and numerous reactions should be considered for describing the composition of the combustion products. Typical description of the process has been achieved using computer models including about 500 reaction mechanisms and 100 chemical species [154]. Upon heating, the oxygen molecule may generate oxygen atoms that react with acetylene as follows:



and/or as follows:

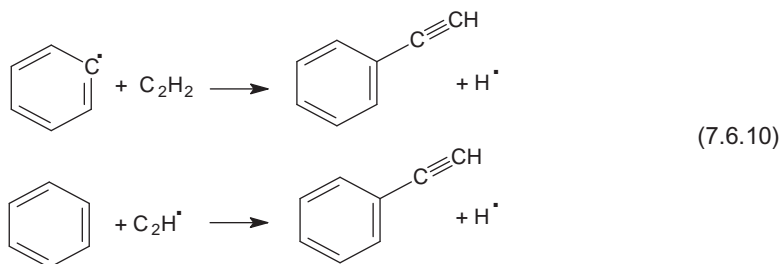


These reactions generate active radicals such as  $\text{CH}_2^{\bullet\bullet}$ ,  $\text{OH}^\bullet$ , and  $\text{H}^\bullet$ . These radicals will react rapidly with acetylene molecules in reactions such as those shown below:

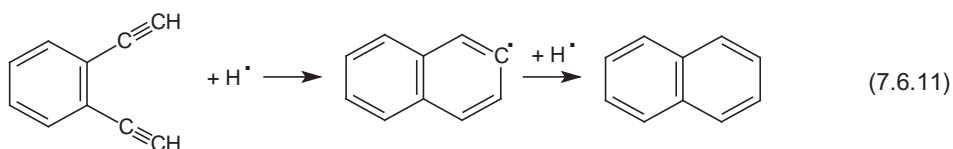


These reactions are continued, with further consumption of oxygen and formation of other intermediate reactive molecules and radicals and finally generating CO,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ .

The formation of PAHs follows numerous routes. One step toward this process starting with already formed benzene or phenyl radical is the generation of ethynylbenzene, which can occur by different reactions, two of them being shown below:



1,2-Diethynylbenzene can be formed from ethynylbenzene by similar reactions. This compound will generate easily naphthalene:



Naphthalene can be generated also starting with buten-3-ynylbenzene, produced, for example, in a termination reaction between  $\text{C}_4\text{H}_3^\bullet$  and phenyl radicals. Reactions of these types will further generate PAHs (see Section 7.8). Kinetic parameters and thermochemical properties for many such reactions are reported in the literature [154,241].

### Other alkynes

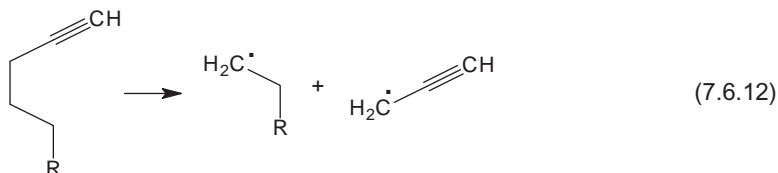
During pyrolysis, propyne undergoes various reactions, depending on temperature, partial pressure (when diluted with an inert gas such as argon), and degree of conversion. Several initiation reactions were considered for the thermal decomposition of propyne. These include one reaction with the generation of propargyl radical ( $\text{HC}\equiv\text{C}-\text{CH}_2^\bullet$ ) and a hydrogen atom, another reaction with the generation of ethynyl  $\text{HC}\equiv\text{C}^\bullet$  and methyl  $\text{CH}_3^\bullet$  radicals, and the third being the isomerization to allene ( $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ ) [244]. Further reactions lead to a complex mixture of unsaturated and aromatic compounds.

Pyrolysis of vinylacetylene has been discussed in connection with acetylene pyrolysis [245]. The pyrolysis of the pure compound also leads to the formation of styrene, which comes from a head-to-head modified Diels–Alder six-member cycloaddition that proceeds through a diradical intermediate. In the  $\text{C}_4\text{H}_4$  system cyclooctatetraene also is seen as an unstable product that isomerizes to styrene. Cyclooctatetraene is formed in concerted, non-free-radical mechanisms, which may proceed both by head-to-head and by head-to-tail eight-member cycloadditions.

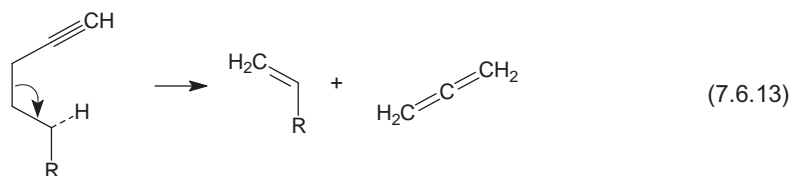
The pyrolysis of 2-methylbut-1-ene-3-yne ( $\text{C}_5\text{H}_6$ ) was studied from 375 °C to 425 °C in a quartz reaction vessel [246]. From 375 °C to 425 °C, the rates of disappearance of reactant and of formation of dimers are second order in  $\text{C}_5\text{H}_6$ . The major product of pyrolysis is a polymer, some dimers accounting for about 3% of the  $\text{C}_5\text{H}_6$  consumed. In addition, toluene and *p*-xylene are produced, their production coming at least in part from the decomposition of the  $\text{C}_5\text{H}_6$  dimers ( $\text{C}_{10}\text{H}_{12}$ ). Also, trace amounts of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  are formed. The reaction mechanism for dimer formation is analogous to that in vinylacetylene pyrolysis, but the dimethylcyclooctatetraene is not detected. Among other compounds detected in the pyrolysate are 2,6-dimethylstyrene and *p*-isopropenyl-toluene.

The results for the pyrolysis of alkynes with a higher number of carbons also have been reported in the literature [178,247]. Pyrolysis starts to be significant for low pressure conditions around 900 K. Three possible mechanisms for the initiation reaction have been suggested. One of these mechanisms

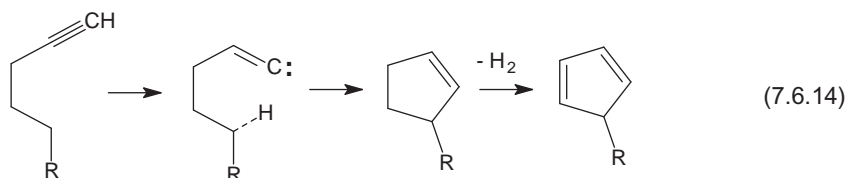
involves a C–C bond cleavage, with the formation of propargyl and alkyl radicals as shown in the following reaction:



Another mechanism is an analog of a retro-ene reaction leading to the formation of an allene and an alkene:

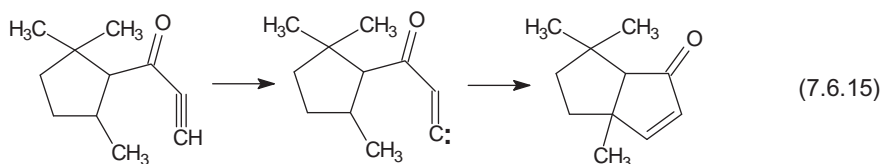


The third mechanism involves the formation of a cyclopentene and further of a cyclopentadiene as shown below:



All three mechanisms were demonstrated to occur for  $\text{C}_5$  to  $\text{C}_8$  alkynes [247]. The products of the initial pyrolysis undergo further reactions generating a mixture of compounds including aromatic molecules.

At high temperatures, acetylenes of the type  $\text{R-C}\equiv\text{C-R'}$  can be in equilibrium with a methylenecarbene of the type  $\text{RR'C=C}^{\bullet\bullet}$  [248]. The presence of a ketone group facilitates this transformation, and the carbene can react further, as shown in the following reaction [249]:



## 7.7. AROMATIC HYDROCARBONS

### General aspects

Aromatic hydrocarbons contain rings of carbon atoms with  $\text{sp}^2$  hybridization, the  $\text{p}_z$  orbitals being involved in  $\pi$  bonds that are stabilized by orbital delocalization and, in addition, by resonance. The number of  $\pi$  electrons necessary to form an aromatic structure is  $2n+4$  (Hückel's rule). Aromatic hydrocarbons show high thermal stability of the aromatic rings. Benzene ( $\text{C}_6\text{H}_6$ ), the typical aromatic hydrocarbon with one ring, has a heat of formation  $\Delta H_f^\circ = +19.81 \text{ kcal/mol}$ , which is, for example, lower with about  $37 \text{ kcal/mol}$  than that for fulvene ( $\text{C}_6\text{H}_6$ ) (heat of formation  $\Delta H_f^\circ = +56.59 \text{ kcal/mol}$ ), where



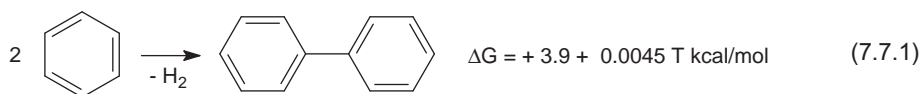
the double bonds are not involved in an aromatic ring. The stability of benzene ring can be proven also by the reaction with hydrogen, where the hydrogenation of the first double bond is endothermic ( $\Delta H^\circ = +5.6$  kcal/mol) while the hydrogenation of the double bond in 1,3-cyclohexadiene is exothermic ( $\Delta H^\circ = -26.5$  kcal/mol). The average dissociation energy of a bond between the carbon atoms in the benzene ring is estimated to be in the range of 132–138 kcal/mol, which is only slightly lower than that for the cleavage of a single double bond. The C–H bond in benzene has a dissociation energy of about +111 kcal/mol. Besides single ring aromatic hydrocarbons, this class includes PAHs. The aromatic rings in PAH can be isolated, for example, in biphenyl, or can be condensed, such as in naphthalene.

Aromatic hydrocarbons are common in nature, being present in crude oil, which can contain as much as 30% of these compounds. Also, the processing of coal to make coke or coal gas generates large quantities of aromatic hydrocarbons. Industrial processing of crude oil and of coal typically is done using pyrolytic techniques at very large scale. Literature information on these techniques is very abundant (see, e.g., [250]).

### Benzene

Benzene is a stable compound during heating. Around 900–1000 °C, depending on the heating time, benzene generates biphenyl, hydrogen, low levels of triphenyl (terphenyl), and low levels of benzo[*f*]phenanthrene [251]. The decomposition of benzene and the formation of biphenyl, hydrogen, and triphenyl as a function of residence time in a flow through experiment at 1000 °C are shown in Figure 7.7.1.

The formation of biphenyl from benzene is a slightly endothermic process:



Considering that the entropy term of reaction 7.7.1 is positive, the heating should not favor the formation of biphenyl. Indeed, the increase in temperature above 1000–1100 °C leads to further decomposition products and a decrease in biphenyl formation [252]. Although the expected mechanism of reaction 7.7.1 is radicalic with the cleavage of a C–H bond and formation of phenyl radicals, it was reported that these radicals were not detected in an experiment monitored using a mass spectrometer [253]. An initiation reaction involving free radicals is indeed not favored thermodynamically, as can be

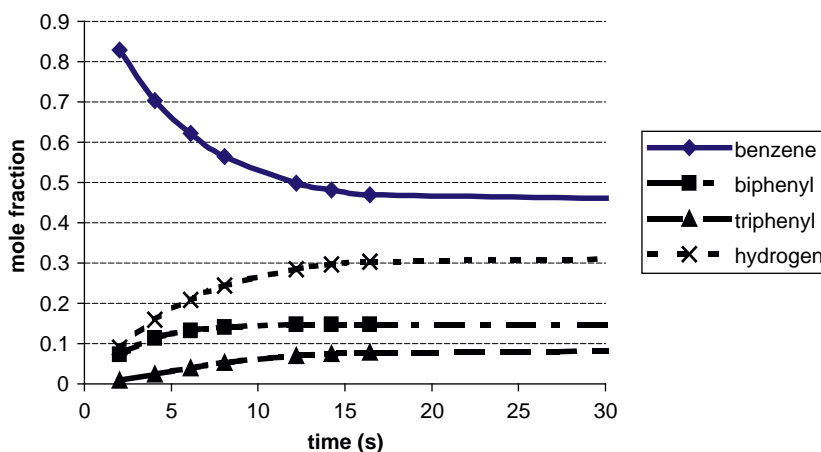
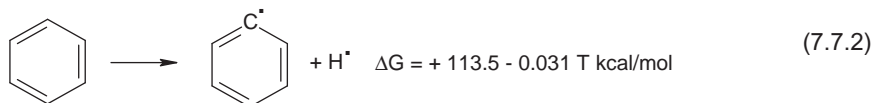
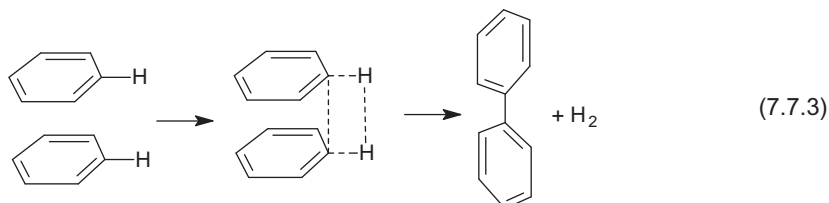


FIGURE 7.7.1. Mole fraction of benzene, biphenyl, triphenyl, and hydrogen as a function of residence time during pyrolysis at 1000 °C in a flow through experiment.

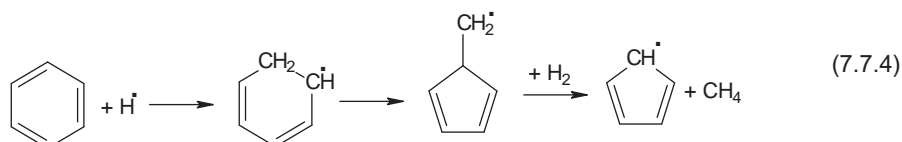
seen from the expression of free enthalpy for this reaction:



A similar mechanism to that of a concerted reaction but with no cyclic transition state is not excluded:



At temperatures above 1200 °C and depending on the partial vapor pressure of benzene (if benzene vapors are diluted with an inert gas such as in shock tube experiments), the decomposition of benzene leads to the formation of acetylene, styrene, diacetylene, as well as traces of triacetylene, vinylacetylene, methane, toluene, etc. A considerable amount of soot (up to 30% of the initial carbon atom concentration) and hydrogen also are released during benzene pyrolysis in temperatures of 1400–2200 K and pressures of 0.25–0.81 atm. Benzene decomposition in these conditions has a second-order rate constant [252] given by the expression  $k = 10^{14.81} \exp(-34.33 \text{ kcal}/RT) \text{ cm}^3/\text{mol/s}$ . The presence of hydrogen atoms in the pyrolysis reaction of benzene may be responsible for the formation of cyclohexadienyl radicals, which further decompose into other radicals such as methylcyclopentadienyl and cyclopentadiene:



Reactions of the type 7.7.4 may be responsible for the formation of traces of methane in benzene pyrolysis, as well as for the formation of toluene and heavier PAHs involving cyclopentadienyl radicals. Cyclohexadienyl radical may follow an alternative path of decomposition besides reaction 7.7.4. Production of acetylene and butadienyl radical ( $\text{C}_4\text{H}_5^\bullet$ ) or formation of two molecules of acetylene and vinyl are among the other potential decomposition paths. The high reactivity of cyclopentadienyl radicals may explain the lack of indications of their presence during the pyrolysis process. Acetylene can be formed also from propargyl radicals generated from benzene in a reaction as follows:



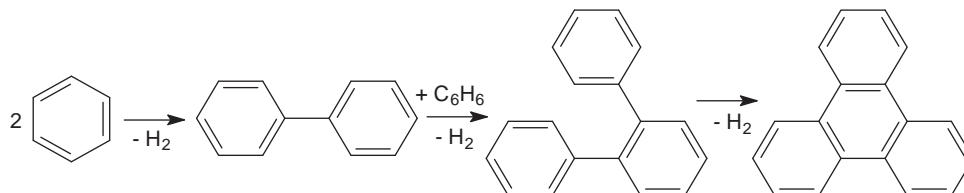
Propargyl radicals can be involved further in termination reactions of the type:



The formation of acetylene in the presence of benzene may lead to the formation of numerous PAHs by a mechanism involving HACA type reactions (see reaction 7.8.3). At temperatures above 1400 °C, the phenyl radicals also can decompose, with the formation of acetylene and but-1-yne-3-enyl radicals ( $\text{HC}\equiv\text{C}-\text{CH}=\text{CH}^\bullet$ ) or the formation of diacetylene and vinyl radicals. An HACA reaction leads to the formation of ethynylbenzene, diethynylbenzene, and further to naphthalene and other PAHs with cluster condensed cycles.

The formation of PAHs in benzene pyrolysates is also the result of reactions similar to reaction 7.7.1, where some steps involving free radicals are possibly present but not directly proven. The formation of

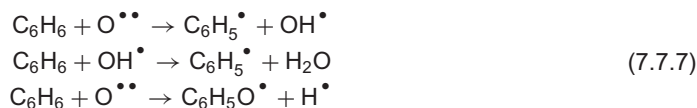
benzo[*l*]phenanthrene, shown below, is a result of this type of reaction:



The formation of heavier PAHs and further condensation reactions are responsible for the soot formation. This soot always contains trace levels of various PAHs. In part for this reason, soot formation from benzene, under various conditions, has been studied in detail [254]. Also, formation of specific PAHs during benzene pyrolysis was studied [251,255,256]. Special substances such as fullerenes were obtained by laser pyrolysis of benzene [257] (see Figure 7.7.2 for the structure of  $\text{C}_{60}$  fullerene).

Formation of carbon nanotubes [258] and of carbon molecular sieves from benzene pyrolysis [259] also were reported. Further details on the formation of PAHs during the pyrolysis of benzene, pure or in mixtures with other compounds, is discussed in Section 7.8.

Benzene flames were thoroughly evaluated and the results have been reported in the literature [155,260–263]. Incomplete burning (fuel rich flames) of benzene generates numerous PAHs through pyrolytic processes. The study of flames at various compositions and temperatures showed that several reactions dominate the burning process. The reactions with oxygen atoms and with  $\text{OH}^\bullet$  radicals are important paths for benzene consumption. The results of these reactions are phenyl and phenoxy free radicals:



The phenoxy radical as well as the reaction of benzene with  $\text{OH}^\bullet$  radicals are the sources of phenol in fuel lean flames of benzene. Besides phenol, the reaction of benzene with  $\text{OH}^\bullet$  produces hydrogen atoms:



The hydrogen atoms react further, forming, for example, a benzyne ( $\text{C}_6\text{H}_4$ ) molecule. The consumption of phenyl radical can take place also with the formation of *p*-benzoquinone and *o*-benzoquinone in a reaction as follows:

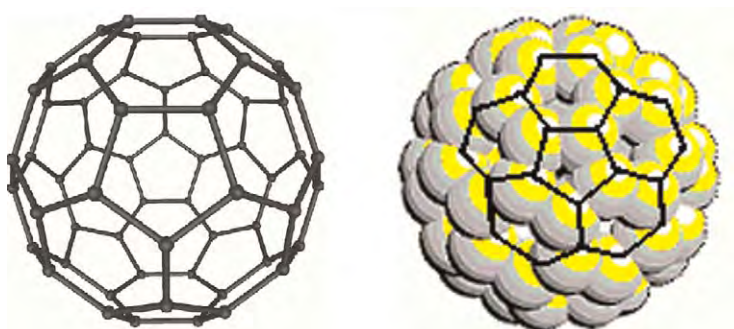


FIGURE 7.7.2.  $\text{C}_{60}$ -fullerene. All bonds are aromatic and of equal length.

Another radical detected in benzene flames is cyclopentadienyl  $C_5H_5^\bullet$ . The formation of cyclopentadienyl radical and of cyclopentadiene is the main result of two unimolecular decompositions shown below [264]:



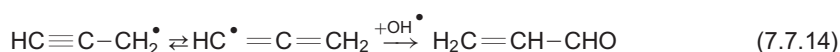
The disappearance of phenoxy radicals from the flame atmosphere can be caused also by the reaction:



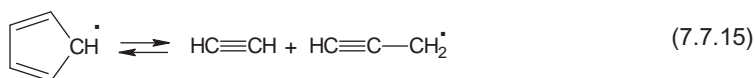
In a reaction similar to 7.7.11, *o*-benzoquinone can generate cyclopentadienone and CO:



Another compound detected in fuel lean benzene flames is acrolein. This compound may originate from the propargyl free radicals formed as a result of benzene decomposition by reaction 7.7.5. Propargyl radicals in a termination reaction with  $OH^\bullet$  radicals can generate acrolein:



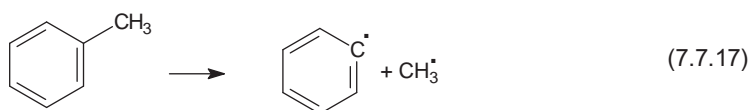
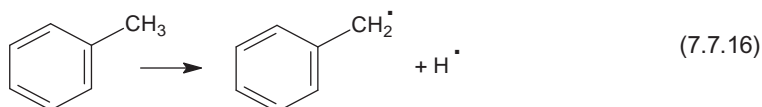
An intermediate compound in benzene flames is acetylene and in stoichiometric flames diacetylene. These compounds together with radicals such as phenyl and cyclopentadienyl are the source of PAHs formed in benzene flames [262]. Acetylene can be formed from cyclopentadienyl radicals (see reaction 7.7.4) by reactions of the type:



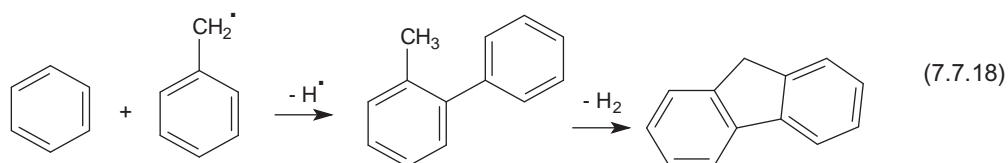
Computer modeling of benzene flame composition is presented in various studies reported in the literature [265,266]. Kinetic parameters of the reactions in benzene flame also have been reported [267–269].

### Toluene

Toluene pyrolysis starts around 1100 K [270]. The initiation reactions dominating toluene pyrolysis are the formation of benzyl radicals and hydrogen atoms and the formation of phenyl and methyl radicals [271]:



A large number of reactions continue these initiations, with formation of benzene and bibenzyl as the main reaction products. At temperatures around 1241 K and 10–15 Torr, naphthalene and phenanthrene start to be formed. At 1315 K and the same pressure range, a variety of PAHs are formed. Besides naphthalene and phenanthrene, these PAHs include chrysene, picene, pyrene, methyl substituted PAHs, phenyl substituted PAHs, and PAHs containing cyclopentane rings. One of the mechanisms of fluorene formation starting with the radicals and molecules formed during toluene pyrolysis is shown below:



Higher PAHs and a considerable amount of soot are generated also upon continuing the heating process. Due to their high molecular weight (and low volatility), some of these PAHs cannot be identified by GC/MS procedures, and LC/MS detection should be employed for their analysis [272]. Hydrogen formation is associated with the pyrolysis process. At temperatures higher than 1477 K, the content of large molecules in the pyrolysate decreases, and small molecules, including  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$ , start to be formed together with carbon [273]. Many kinetic parameters for toluene pyrolysis are reported in the literature [274]. A detailed kinetic model using 262 reactions and 87 molecular and radicalic species was developed for the identification of the main mechanisms. For these mechanisms literature data and estimations for the kinetic parameters, including those necessary in Arrhenius equation  $k = A T^n \exp(-E^a/RT)$ , as well as Troe parameters [274] were used. This large number of reactions was necessary to obtain agreement with experimental data regarding pyrolysate compositions in the temperature range 1200–1900 K and pressures between 27 bar and 45 bar. Various other studies were performed on toluene, including pyrolysis in the presence of acetylene [271], other hydrocarbons [275], binary mixtures with methanol or ethanol [276], and added hydrogen [277]. Results for pyrolysis of toluene at supercritical conditions (critical temperature being 319 °C and critical pressure 41 atm) were also reported [278]. Oxidative pyrolysis results and computer modeling of soot formation in shock tubes in the presence of oxygen were also published [89].

As previously indicated, pyrolysis of toluene and of other alkyl substituted aromatic hydrocarbons generates hydrogen and soot. The addition of hydrogen during pyrolysis modifies the course of the pyrolytic process, considerably decreasing the amount of soot. This type of pyrolysis (in the presence of hydrogen and usually in the presence of catalysts) is widely used in oil processing (hydrocracking). Pyrolysis of toluene in the presence of hydrogen generating methane and benzene has been studied as a model reaction for pyrolysis/hydrogenation process [279].

### Other single ring aromatic hydrocarbons

Pyrolysis of many other monocyclic aromatic hydrocarbons with various substituents was evaluated and the results are reported in the literature. Among these are xylenes [280] and decylbenzene [281]. *p*-Xylene, for example, during pyrolysis above 800 °C forms among other constituents a *p*-cyclophane:

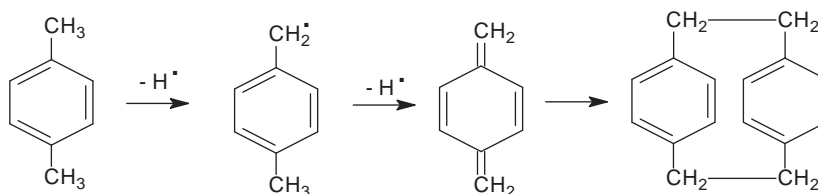
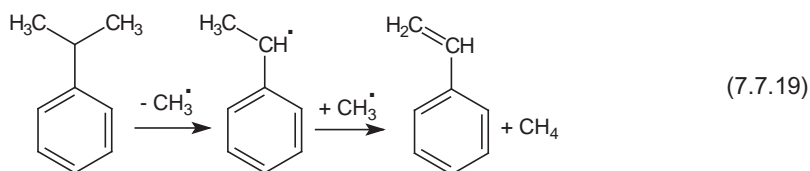


TABLE 7.7.1. Yields of various pyrolysis products from cumene, *p*-cymene, and  $\alpha$ -methylstyrene obtained at 800°C on Vycor glass with a contact time of about 3.9 s and collected in a cold acetone trap obtained [282]

Compound	Yield %		
	<i>p</i> -Cymene	Cumene	$\alpha$ -Methylstyrene
Benzene	5.8	27.0	16.2
Toluene	11.1	3.7	5.2
Xylene	3.1	0.6	0.6
Styrene	7.2	18.7	13.8
Cumene	—	24.2	—
$\alpha$ -Methylstyrene	1.7	2.8	24.3
<i>p</i> -Cymene	23.4	—	—
<i>p</i> -Methylstyrene	22.5	—	0.6
Indene	1.6	2.5	7.9
<i>p</i> - $\alpha$ -Dimethylstyrene	4.5	—	—
Naphthalene	3.9	6.9	9.0
2-Methylnaphthalene	2.7	0.7	1.4
1-Methylnaphthalene	0.3	0.6	1.5
Biphenyl	0.3	1.1	2.6
2-Vinylnaphthalene	0.8	0.3	0.4
Acenaphthylene	0.5	0.6	1.0
Fluorene	0.2	1.2	1.6
Phenanthrene	2.1	4.0	3.8
Total volatiles	91.7	94.9	89.9
% vs. initial material	35.3	41.4	46.0

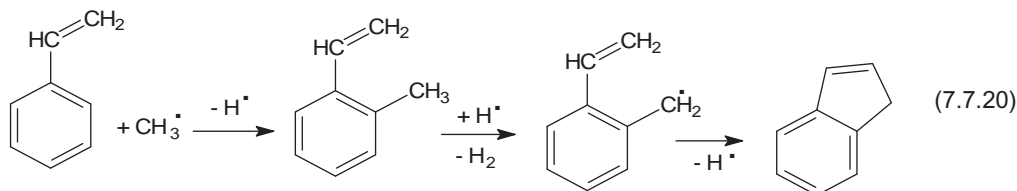
Among other single aromatic ring hydrocarbons that were studied regarding their pyrolysis products are isopropylbenzene (cumene), 1-methyl-4-(1-methylethyl)benzene (*p*-cymene), and  $\alpha$ -methylstyrene [282]. These compounds were pyrolyzed at 800°C on Vycor glass with a contact time of about 3.9 s. The yields of various pyrolysis products collected in a cold acetone trap from these three parent compounds are shown in Table 7.7.1.

In addition to the compounds from Table 7.7.1, gaseous, noncondensable products such as CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and H<sub>2</sub> were generated during pyrolysis, and together with some char, they account for a large proportion of the initial amount of parent compound. Pyrolysis of cumene, *p*-cymene, and  $\alpha$ -methylstyrene takes place with formation of free radicals. Starting for example with cumene, a C—C bond with both carbons having a sp<sup>3</sup> hybridization is the most likely to suffer a cleavage, as shown in the following reaction:



Further reactions take place involving the free radicals generated in reaction 7.7.19. For example, formation of indene in the pyrolysate can be explained by a sequence of several reactions involving free

radicals, as shown below:

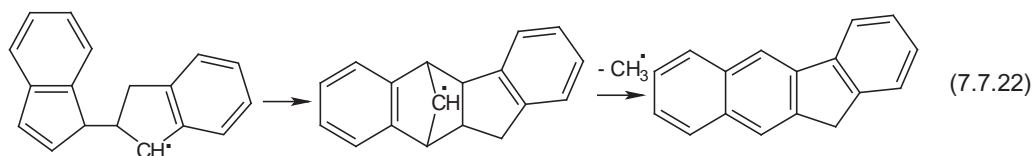


Shock wave studies of the pyrolysis of ethylbenzene, isopropylbenzene, *tert*-butylbenzene, and styrene also were performed [283]. During ethylbenzene pyrolysis, a primary C–C bond split is dominant. The rate of decomposition follows the expression

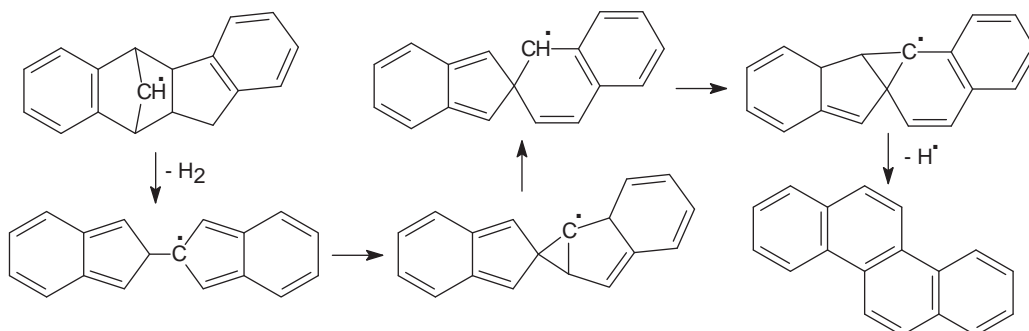
$$k = 10^{15.55} \exp\left(\frac{-306.7(\text{kJ/mol})}{RT}\right) \text{s}^{-1} \quad (7.7.21)$$

Besides toluene, other pyrolysate components include styrene, benzene, and acetylene. Further pyrolysis leads to the formation of soot and some amount of PAHs. The reaction paths for PAH formation are very complex. They involve the reaction products from initial stages of pyrolysis such as acetylene, benzene, and styrene. The same C–C bond split is dominant during isopropylbenzene and *tert*-butylbenzene pyrolysis.

Pyrolysis products of other aromatic hydrocarbons containing aliphatic substituents also were evaluated. Special attention was given to indene ( $\text{C}_9\text{H}_8$ ), which contains a cyclopentadienyl cycle fused with a benzene ring. The pyrolysis of this compound is of particular interest for the understanding of the formation of PAHs containing five-member rings from other hydrocarbons. Indene pyrolysis is somewhat different from that of hydrocarbons containing only fused aromatic cycles. Indene starts decomposing around  $650^\circ\text{C}$  with typical formation of soot, hydrogen, and PAHs. The major PAHs generated during indene pyrolysis are  $\text{C}_{18}\text{H}_{12}$  isomers (chrysene, benzo[*a*]anthracene and benzo[*c*]phenanthrene), two  $\text{C}_{17}\text{H}_{12}$  isomers (benzo[*a*]fluorene and benzo[*b*]fluorene), and two  $\text{C}_{10}\text{H}_8$  isomers (naphthalene and benzofulvene). The reaction pathway for these products starts with the formation of indenyl radical that further reacts with indene producing a resonance-stabilized radical (similar to cyclopentadienyl radical reacting with cyclopentadiene in reaction 7.5.3). The intermediate radical can react further by intramolecular addition producing a bridged structure that leads to the formation of  $\text{C}_{17}\text{H}_{12}$  products. The formation of 11H-benzo[*b*]fluorene ( $\text{C}_{17}\text{H}_{12}$ ) by this mechanism is shown in the following reactions [284]:



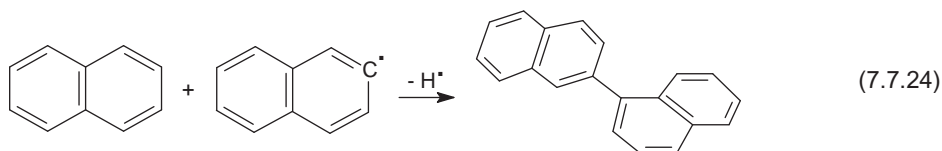
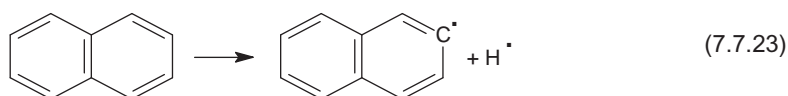
By  $\beta$ -scission and hydrogen elimination the same intermediate bridged radical from reaction 7.7.22 generates biindenyl, which leads to the formation of  $\text{C}_{18}\text{H}_{12}$  products by a ring condensation mechanism analogous to that proposed for cyclopentadiene to form naphthalene (see reaction 7.5.5). Formation of chrysene is given below as an example:



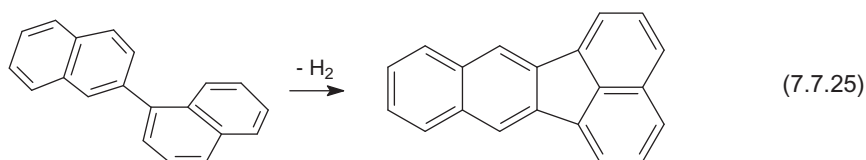
Among other compounds with both aromatic and aliphatic moieties that were studied regarding their pyrolysis are 1,2-dihydronaphthalene [285], cyclobutene substituted aromatic hydrocarbons [286], and alkyl–aromatic hydrocarbons with industrial applications [287,288]. Also, pyrolysis of mixtures of various aromatic hydrocarbons was reported in the literature [289–291].

### Aromatic hydrocarbons with more than one aromatic ring

Pyrolysis of the aromatic hydrocarbons with more aromatic rings (fused or not) takes place by mechanisms similar to those for benzene or toluene. The hydrocarbons such as naphthalene, anthracene, pyrene, and fluoranthene generate soot and a mixture of heavier aromatic hydrocarbons (PAHs) during pyrolysis [292]. The PAHs in these mixtures consist of molecules with both coplanar and noncoplanar rings. For example, in the case of naphthalene one of the first processes taking place during pyrolysis is the formation of naphthyl radicals. These radicals can generate a noncoplanar 2-naphthyl-naphthalene in a termination reaction or in a reaction with naphthalene and elimination of a hydrogen atom, as shown below:



The formation of bay areas in the resulting molecules resulting in noncoplanar structures may lead to some weakening of the covalent bonds that form that bay area since optimum delocalization and resonance of the  $\pi$  electron system imply a planar structure. For this reason, across the bay areas the cyclodehydrogenation reactions are common. Formation of benzo[*k*]fluoranthene leading to a coplanar molecule is such a dehydrogenation reaction:



Separate pyrolysis of 1,2'-binaphthyl at temperatures above 1000 °C leads to the formation of various compounds including C<sub>60</sub> and C<sub>70</sub> fullerenes [293]. This explains the formation of low levels of fullerenes during naphthalene pyrolysis [294].

A study on naphthalene pyrolysis using shock wave compression with shock temperatures between 830 K and 1660 K provides information on a wider range of thermal conditions [295]. Pyrolysis generated an insoluble dark matter (with a high content of carbon) as a major product and low levels of PAHs as shown in Table 7.7.2 [295]. Hydrogen was generated also in this pyrolysis process.

The secondary PAHs generated in the shock-induced pyrolysis experiment on naphthalene [295] included various molecules in which the initial compound had been methylated, phenylated, naphthylated, or dehydrogenated. Table 7.7.3 lists these PAHs determined by GC/MS in the soluble part of the pyrolysate of naphthalene.

Experiments similar to that for naphthalene were reported for anthracene, pyrene, and fluorene [295]. Table 7.7.4 lists the PAHs analyzed in the pyrolysates of anthracene obtained using shock-induced pyrolysis in the temperature range 730–1370 K [295].



TABLE 7.7.2. Results of shock-induced pyrolysis of naphthalene as reported in [295]

Property				
Shock temperature (K)*	<b>830</b>	<b>1130</b>	<b>1470</b>	<b>1660</b>
Conversion (%)	20	77	92	99
Dark matter (%)	17	71	85	99
1-Methylnaphthalene (%)	0.009	0.24	0.43	0.004
2-Methylnaphthalene (%)	0.021	0.29	0.55	0.007
Dimethylnaphthalene (%)	0.002	0.052	0.086	0.001
Total of methylation products (%)	0.034	0.613	1.108	0.013
1-Phenylnaphthalene (%)	0.002	0.021	0.04	0
2-Phenylnaphthalene (%)	0.004	0.004	0.008	0.001
Total of phenylation products (%)	0.007	0.089	0.176	0.001
1,10-Binaphthyl (%)	0.023	0.44	0.4	0
1,20-Binaphthyl (%)	0.064	0.9	1.1	0
2,20-Binaphthyl (%)	0.054	0.65	0.93	0
Total of naphthylation products (%)	0.153	2.221	2.823	0
Other products (%)	0.022	0.375	0.636	0.005
Secondary PAHs (%)	0.216	3.289	4.743	0.019

\*Other shock-induced pyrolysis parameters are described in [295].

TABLE 7.7.3. List of secondary PAHs identified during naphthalene pyrolysis in a shock induced pyrolysis experiment [295]

Compound	Compound	Compound
Acenaphthene	Coronene	1-Methylnaphthalene
Acenaphthylene	1,2-Dimethylnaphthalene	2-Methylbiphenyl
Anthracene	1,3-Dimethylnaphthalene	2-Methylnaphthalene
1,1-Binaphthyl	1,4-Dimethylnaphthalene	3-Methylbiphenyl
1,2-Binaphthyl	1,5-Dimethylnaphthalene	Methylpyrene
2,2-Binaphthyl	1,6-Dimethylnaphthalene	Naphthalene
Benzo[a]anthracene	1,7-Dimethylnaphthalene	Naphthalene dimer
Benzo[a]pyrene	2,3-Dimethylnaphthalene	1-phenylnaphthalene
Benzo[b]fluoranthene	2,6-Dimethylnaphthalene	2-Phenylnaphthalene
Benzo[ghi]perylene	2,7-dimethylnaphthalene	Perylene
Benzo[k]fluoranthene	Fluoranthene	Phenanthrene
Biphenyl	Fluorene	Pyrene
Chrysene	Indeno[1,2,3-cd]pyrene	Ternaphthyl

TABLE 7.7.4. List of compounds identified during anthracene pyrolysis in a shock-induced pyrolysis experiment [295]

Compound	Compound	Compound
Acenaphthylene	Bibenzo[ah]anthracene	2-Methylnaphthalene
Anthracene dimer	Fluorene	Naphthalene
Benzo[a]anthracene	1-Methylnaphthalene	Pyrene
Bianthryl	2-Methylbiphenyl	

TABLE 7.7.5. List of compounds identified during pyrene pyrolysis in a shock-induced pyrolysis experiment [295]

Compound	Compound	Compound
Acenaphthene	Bipylene	Methylpyrene
Acenaphthylene	Chrysene	Naphthalene
Anthracene	Dimethylpyrene	1-Phenylnaphthalene
Benzo[a]anthracene	Fluoranthene	2-Phenylnaphthalene
Benzo[a]pyrene	Fluorene	Perylene
Benzo[b]fluoranthene	Indeno[1,2,3- <i>cd</i> ]pyrene	Phenanthrene
Benzo[ <i>ghi</i> ]perylene	1-Methylnaphthalene	Pyrene dimer
Benzo[ <i>k</i> ]fluoranthene	2-Methylnaphthalene	

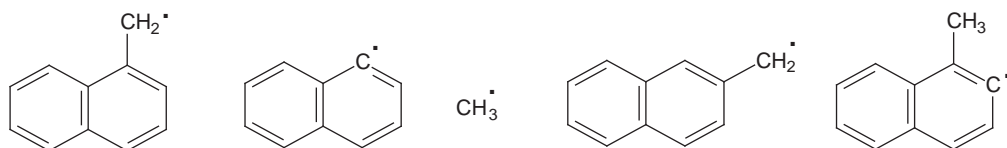
TABLE 7.7.6. List of compounds identified during fluorene pyrolysis in a shock-induced pyrolysis experiment [295]

Compound	Compound	Compound
Acenaphthene	Fluoranthene dimer	Naphthalene
Acenaphthylene	Fluorene	1-Phenylnaphthalene
Benzo[b]fluoranthene	1-Methylnaphthalene	2-Phenylnaphthalene
Bifluoranthene	2-Methylnaphthalene	Perylene
Dimethylfluoranthene	Methylfluoranthene	Phenanthrene

The experiments for pyrene were performed in the temperature range 79–1460 K and those for fluorene in the temperature range 720 and 1480 K. The list of PAHs in the pyrolysate of pyrene is given in Table 7.7.5 and that for fluorene in Table 7.7.6.

The identification of individual PAHs in pyrolysates is important up to 5–6 aromatic rings. Above this number of rings, individual PAH identification in a mixture starts to be more problematic. The use of GC separation becomes a problem due to the low volatility of heavier compounds, and HPLC technique must be utilized for separation [272]. Identification of each PAH is further complicated when only a UV detection is available. LC/MS techniques are desirable for the identifications of PAHs with more than five aromatic rings [296–298].

Aromatic molecules with more than one ring and containing alkyl groups are prone to complicated pyrolysis pathways and the formation of complex pyrolysis products [299,300]. These pyrolysis products consist mainly of H<sub>2</sub>, carbon (soot), and a variety of PAHs. Pyrolysis of 1-methylnaphthalene, for example, generates in the initiation reaction the following radicals:



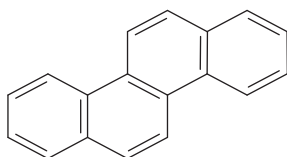
No single aromatic ring compounds and no acetylene are detected during the pyrolysis of 1-methylnaphthalene around 600 °C, indicating that the aromatic rings remain intact under these conditions. Further reactions involving the free radicals previously indicated generate a considerable number of PAHs. From the PAHs with two to seven rings, 37 individual ones were

reported as being present in the pyrolysate [299]. Pyrolysis studies were done also for other aromatic compounds including corannulene, 11,12-benzofluoranthene, anthracene, and benzo[c]phenanthrene [301,302].

## 7.8. FORMATION OF POLYCYCLIC AROMATIC HYDROCARBONS DURING PYROLYSIS AND COMBUSTION OF HYDROCARBONS

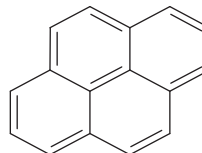
### General aspects

PAHs are compounds of considerable concern for health and environmental issues. For example, benzo[a]pyrene is a known pre-carcinogen. By enzymatic metabolism, benzo[a]pyrene is transformed into a diol epoxide that intercalates in the DNA by covalently bonding to the guanine nucleobase. This process distorts the DNA and induces mutations. PAHs found in the environment are formed from various sources, an important one being hydrocarbon pyrolysis that takes place in common activities such as fossil fuel combustion and thermal processing of crude oil, of various oil fractions, and of coal. PAHs are typically present in the soot formed by incomplete burning and in the carbon depositions generated in industrial pyrolytic processes. There are several types of PAHs. The main types include those containing: (a) sequentially connected aromatic rings (e.g., naphthalene, anthracene, phenanthrene, and chrysene), (b) cluster connected aromatic rings (e.g., pyrene and benzo[ghi]perylene), (c) aromatic rings and unsaturated five-member rings with three fusing sites, and (d) aromatic rings and CH<sub>2</sub> bridges with four fusing sites. Examples with the general formulas (number of carbons and hydrogens) and special notations for the PAHs in these four categories are shown below.



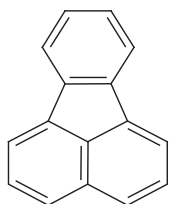
chrysene A<sub>4</sub>

Sequentially connected PAHs with *n* rings  
C<sub>2</sub>H<sub>4</sub> + *n*(C<sub>4</sub>H<sub>2</sub>) indicated as A<sub>*n*</sub>



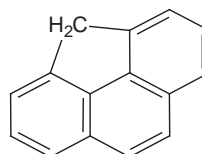
pyrene A<sub>4</sub>D<sub>2</sub>

Cluster connected PAHs with *n* rings and *m* internal  
carbons C<sub>2</sub>H<sub>4</sub> + *n*(C<sub>4</sub>H<sub>2</sub>) - *m*(CH) A<sub>*n*</sub>D<sub>*m*</sub>



fluoranthene A<sub>3</sub>D<sub>0</sub>C<sub>1</sub>

PAHs containing unsaturated five-member  
rings and three fusing sites  
C<sub>2</sub>H<sub>4</sub> + *n*(C<sub>4</sub>H<sub>2</sub>) - *m*(CH) + *l*(C<sub>2</sub>) A<sub>*n*</sub>D<sub>*m*</sub>C<sub>*l*</sub>



4H-cyclopenta[def]phenanthrene A<sub>3</sub>D<sub>0</sub>Y<sub>1</sub>

PAHs containing CH<sub>2</sub> bridges to form  
five member rings with four fusing sites  
C<sub>2</sub>H<sub>4</sub> + *n*(C<sub>4</sub>H<sub>2</sub>) - *m*(CH) + *k*(C) A<sub>*n*</sub>D<sub>*m*</sub>Y<sub>*k*</sub>

Some PAHs such as corannulene (dibenzo[ghi,mno]fluoranthene) are not included in these types of PAHs. Also, several substitutions are possible on the cyclic skeleton, including those with alkyl, alkenyl, alkynyl, or aryl groups (not mentioning other functional groups such as halogen, OH, and epoxide). These substitutions extend the possibilities of PAH structures to a higher complexity. There is no precise limit for the number of rings in a PAH molecule. However, compounds with more than eight connected rings (such

as benzo[*a*]coronene, phenanthro[5,4,3,2-*efgh*]perylene, benzo[*pqr*]naphtho[8,1,2]perylene, or benzo[*ghi*]naphtho[8,1,2]perylene) are very difficult to identify as individual compounds [303].

### PAH formation during pyrolysis

The generation of PAHs by pyrolysis (or oxidative pyrolysis in flames) from single hydrocarbons or from a mixture of hydrocarbons involves numerous reactions. Even starting with methane (see Section 7.1), continuous heating leads to the formation of numerous chemical species and the mechanism of PAH formation becomes very complex. For this reason, typical studies utilize computer programs that allow the modeling of the pyrolysis or of the burning process. These programs may target simulation of data regarding the expected chemical composition of the flame or of the pyrolysate. In this case, the models take into consideration a large number of chemical reactions and their kinetic and thermodynamic parameters. The necessary thermodynamic and kinetic parameters are either obtained from the literature or optimized to fit the model. The agreement (or disagreement) of the calculated data with the experimental values for the composition of the flame or of the pyrolysate is used to understand which reactions and which compounds play an important role in the process and allows predictions regarding the PAHs formation. Other models target the soot formation [304]. A computer-generated model molecule built around corannulene, which leads to the formation of fullerenes, is shown in Figure 7.8.1.

Typical formation of PAHs occurs when the pyrolysis temperature is above a specific value (depending on the hydrocarbon) and when heating is performed for extended periods of time (see Sections 7.1–7.7). Multiple reaction paths for PAHs formation may have the same compound as origin. The contribution of each path to the final pyrolysate composition is not equal and depends on both parent and resulting compounds. Under different pyrolysis conditions (temperature, pressure,

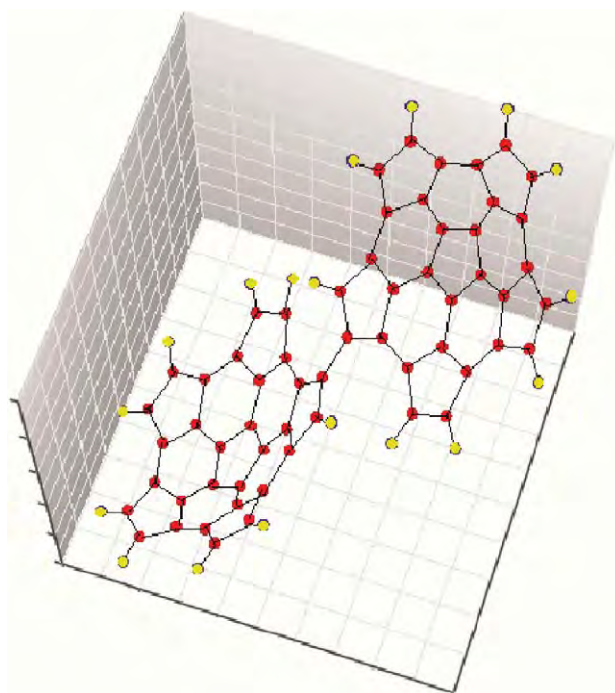
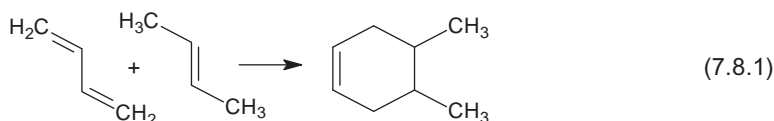


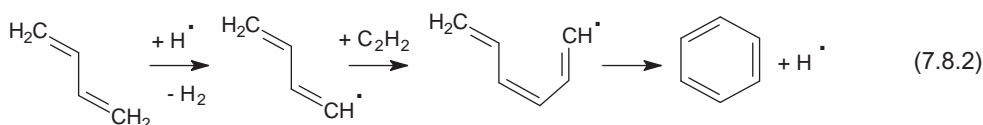
FIGURE 7.8.1. Computer-generated model of a molecule that leads to the formation of fullerenes (dark dots are carbons, gray dots are hydrogens).

pyrolysis time, presence of other hydrocarbons, etc.) the significance of a specific reaction path varies even for the same initial and final compound. In spite of this complexity, some common intermediate compounds were found in many pyrolytic processes leading to the formation of PAHs and soot [50,52,53,154].

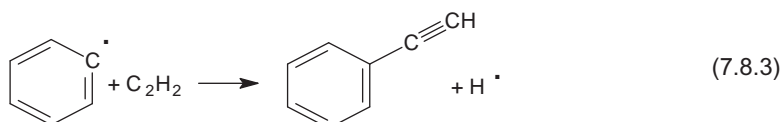
The first stages of most pyrolysis processes occur with formation of fragments with a lower molecular weight compared to that of the parent molecule. This process typically includes the formation of free radicals and of special types of molecules that are thermally stable but highly reactive (such as acetylene). The increase in the molecular weight from the parent compound to the resulting PAH indicates that at some points along the reaction chain there must be interactions between fragments and formation of compounds with a molecular weight higher than that of the parent molecule. The interacting fragments can be molecular species or free radicals. Typical for the increase in the molecular weight are condensation reactions (e.g., Diels–Alder type) when the interaction takes place between molecular species (condensation of molecular species can also take place by radicalic mechanisms as seen in reactions 2.5.2–2.5.4). This explains why an important role in PAH formation is played by molecules such as acetylene, vinylacetylene, butadiene, isoprene, cyclopentadiene, methylcyclopentadiene, and indene, which contain double and triple bonds. As an example, the Diels–Alder type condensation between butadiene and 2-butene is shown below:



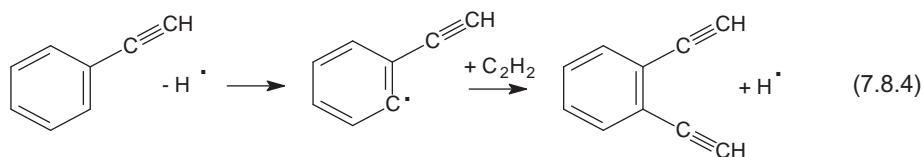
Reactions between free radicals and neutral molecules also can lead to an increase in the molecular weight. For example, radical additions to double or triple bonds between two molecules lead to larger molecules, as shown for example in reaction 7.3.12 in which methylcyclopentene is formed from an allyl radical and propene. Some reactions may involve free radicals and neutral molecules, as shown below for the reaction between butadiene and acetylene:



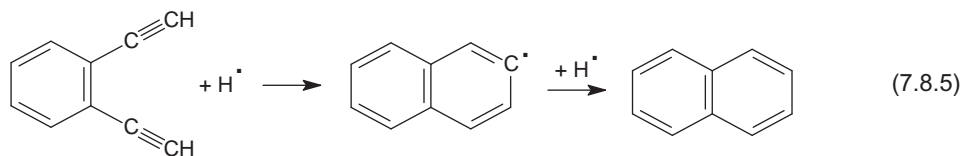
Hydrogen abstraction by smaller radicals from larger molecules, which is a common process in radical interactions, leads to the formation of larger radicals that are typically more stable than small radicals. The most common small free radicals involved in transfers are hydrogen atoms,  $\text{CH}_3^\bullet$ , and  $\text{C}_2\text{H}_5^\bullet$ . In reaction 7.8.2, for example, butadienyl radical is generated by interaction with a  $\text{H}^\bullet$  atom, but the same role can be played by methyl  $\text{CH}_3^\bullet$  or other common small free radicals formed during pyrolysis. The larger free radicals further interact to form larger molecules by different processes. A common process is free radical termination. The reaction between two phenyl radicals produces biphenyl, as shown in reaction 7.7.1. The reaction of a free radical with an acetylene molecule has been found to be an important reaction leading to PAH formation. This reaction is known as HACA (hydrogen abstraction, acetylene addition) and an example of such reaction is shown below [305]:



The presence of acetylene in many pyrolytic reactions taking place at temperatures above 900–1000 °C is favored by the thermal stability of this compound. The HACA type reaction can continue with the resulting molecules from a previous step. For example, ethynylbenzene from reaction 7.8.3, after further reaction with the hydrogen atoms, continues the HACA process:

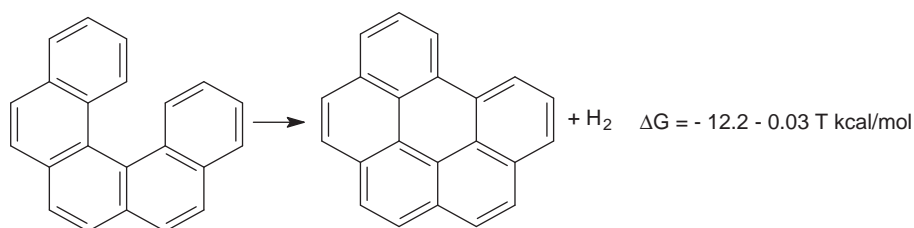


Some reactions leading to the formation of larger molecules already involve aromatic compounds (see Section 7.7). However, the formation of larger molecules alone during pyrolysis is not sufficient to produce PAHs. Aromatization reactions taking place by various mechanisms are necessary for this result. Some of the aromatization reactions involve free radicals, as shown below for the formation of naphthalene:

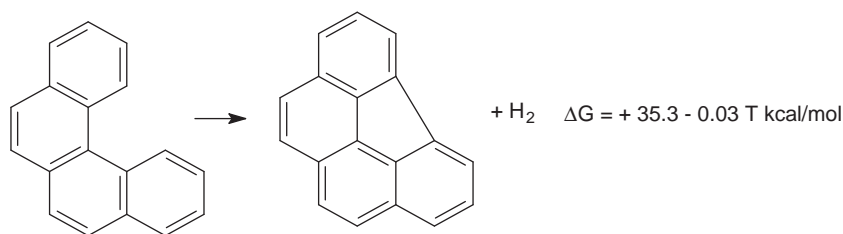


The free radicals of larger molecules are typically generated by interactions with smaller radicals, as previously indicated ( $\text{H}\cdot$  in reactions 7.8.5). Other aromatization reactions involve eliminations of smaller molecules. Several reactions with hydrogen elimination and formation of aromatic rings were previously discussed (see, e.g., reaction 7.5.6).

Exceptional energetic stability of the benzene aromatic system is the main driving force in the aromatization process. When more aromatic rings are formed, the conjugation and resonance energy that stabilizes aromatic structures favors the production of these molecules. The generation along the chain of reactions of molecules with bay areas destabilizes to a certain extent the surrounding bonds and leads to an easier elimination of small fragments (such as hydrogen molecules). The reactions are favored not only due to the change in enthalpy, but an entropic contribution is also brought by the hydrogen elimination (31.23 cal/T/mol). The entropic factor is more important when the temperature increases. The dehydrogenation reaction of dibenzo[*cg*]phenanthrene into benzo[*ghi*]perylene is given below as an example (thermodynamic values calculated using MOPAC 7 with AM1 parameters [306]):

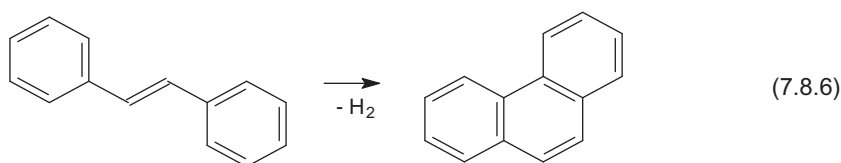


Hydrogen elimination from a molecule with a five-carbon bay area is exemplified for the transformation of benzo[*c*]phenanthrene into benzo[*ghi*]fluoranthene:



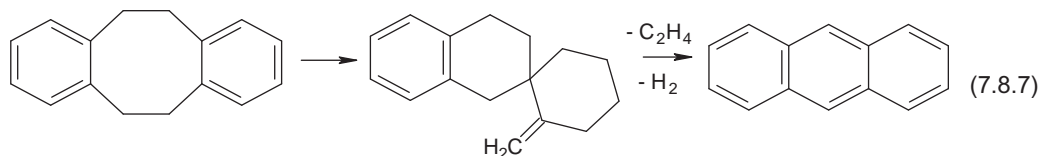
This reaction begins to be thermodynamically favorable only at temperatures above 800 °C since the ring strain energy of benzo[ghi]fluoranthene has a positive value as compared to benzo[c]phenanthrene with no ring strain.

A common procedure for the preparation of PAHs also driven by the increased stability of aromatic systems starts with stilbene type compounds.



Similarly, benzo[c]phenanthrene can be synthesized by pyrolysis of 2-(2-phenylvinyl)-naphthalene [307–313].

The high stability of aromatic rings leads to the formation of PAHs by the pyrolysis of many less stable compounds. One example is the formation of anthracene from 5,6,1,12-tetrahydridibenzo[ae][8]annulene or 5,6,1,12-tetrahydridibenzo[ae]cyclooctatetraene, as shown in the following reaction (see also mechanism 2.4.6):

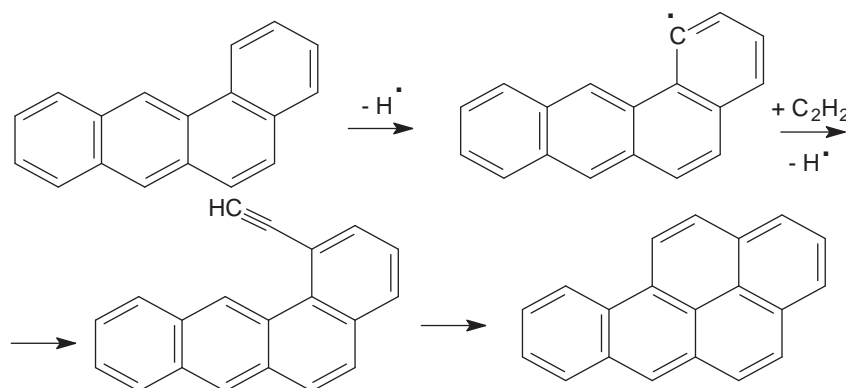


Typical literature information regarding the generation of PAHs provides results with a specified starting compound, for example, ethylene [154], acetylene [241,223], propane [50,52,53], acetylene and benzene [255], toluene [271], toluene and *n*-heptane [89,314], or cyclohexane [315]. This approach also has been taken in Sections 7.1–7.7 of this book, where some results on PAH formation were discussed beginning with individual compounds.

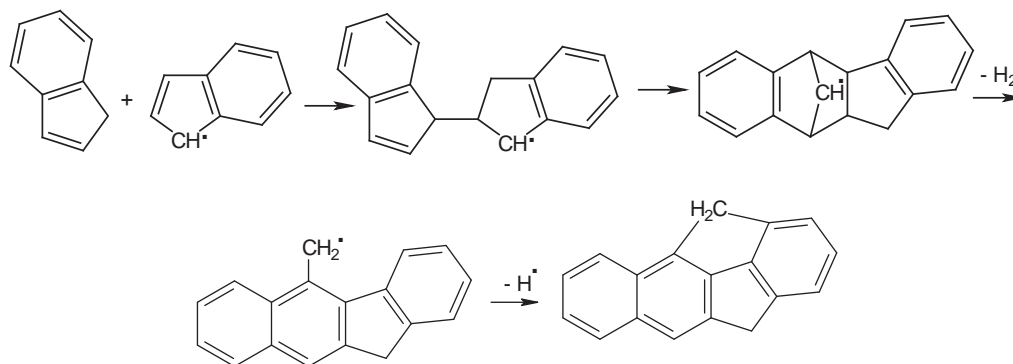
Considering the main types of PAHs generated in pyrolytic processes from hydrocarbons, several general characteristics can be noticed. For sequentially connected PAHs, their formation can proceed by various mechanisms. These include mechanisms involving acetylene molecule with or without an initial compound containing aromatic rings. Acetylene itself produces benzene during pyrolysis (see reaction 7.6.4). Reactions 7.8.3–7.8.5 show the production of naphthalene in a sequence of HACA reactions. Naphthalene can react further in a manner similar to benzene (via naphthyl free radicals and HACA mechanism) to form anthracene and phenanthrene. Reactions involving cyclopentadienyl radicals (see reaction 7.6.5) or indenyl radicals can generate sequential PAHs. However, reaction pathways to the formation of PAHs including only successive growth steps involving small hydrocarbons are not sufficient for explaining the measured induction times of soot formation, more complex paths accounting better for the process.

For the formation of cluster connected PAHs, in addition to the mechanisms indicated for sequential PAHs, elimination of small molecules in potentially formed bay areas of intermediate compounds is usually necessary. Also, eliminations and rearrangements involving side-chain substituents are

common paths for the generation of these types of compounds, as shown in the following reactions for benzo[a]pyrene formation from benzo[b]phenanthrene:

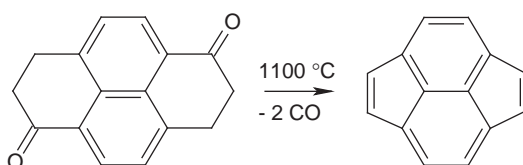


The presence of side-chain substituents, rearrangements, and elimination reactions are also common for the formation of PAHs containing five-carbon rings. During the formation of PAHs with five-carbon rings and of those containing  $\text{CH}_2$  bridges, there are numerous reaction paths that can be followed. The participation of cyclopentadiene and indene as intermediate compounds in PAH formation is one of these paths. Formation of indene and methylinene from cyclopentadiene is shown by reaction 7.5.4. Similar reactions involving a larger number of rings is shown for indene leading to 11H-benzo[b]fluorene (see reaction 7.7.17). Different PAHs can result from the same initial compounds, as shown by comparing reaction 7.7.17 with the following reaction:

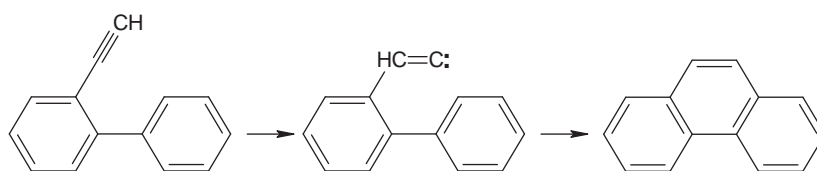


Other paths for the formation of PAHs with five-carbon rings involve aromatic hydrocarbons with side-chain substituents, as shown, for example, with the formation of fluorene in reaction 7.7.15.

Besides the formation of classes of PAHs, specified target compound formation is discussed in the literature [316]. Also, PAHs are sometimes intentionally synthesized [317]. Procedures for this purpose include various elimination reactions with suitable leaving groups such as  $\text{CO}$ ,  $\text{HCl}$ ,  $\text{SO}_2$ , carbene insertion reactions, thermal rearrangement of carbon skeleton, etc. Several of these reactions were previously discussed (for  $\text{SO}_2$  elimination during sulfone pyrolysis, see Section 22.4). Two more specific examples are shown below:







### PAH formation in flames

The formation of PAHs by pyrolysis is closely related to the formation of PAHs in flames. Incomplete burning of many fuels generates soot and PAHs, the process being a combination of pyrolysis and combustion. Acetylene flames were of particular interest since they offer a model for soot and PAH formation. In addition, acetylene flames are used in welding. Very frequently, the formation of PAHs by pyrolysis was studied at the same time with studies of their formation in flames [53,88,154,223,318].

As previously shown for the pyrolytic formation of PAHs, the generation of free radicals during the process plays an important role in the reaction mechanisms. In the presence of oxygen (air), the number of free radicals participating in the reactions is considerably increased. The oxygen molecules react with the initial free radicals generated by heating of the fuel following a multitude of reactions. A few of the reactions from flames involving exclusively oxygen and hydrogen are listed in Table 7.8.1, where some kinetic parameters are indicated for the formula  $k = A T^n \exp[-E^\ddagger / (RT)]$ .

TABLE 7.8.1. Model reactions involving hydrogen and oxygen atoms pertinent to flame reaction mechanisms [154]

Reaction	A	n	$E^\ddagger$ (kcal/mol)
$H^\bullet + O_2 \rightarrow O^\bullet + OH^\bullet$	$8.30 \times 10^{13}$		14.413
$O^\bullet + H_2 \rightarrow H^\bullet + OH^\bullet$	$5.00 \times 10^4$	2.67	6.29
$OH^\bullet + H_2 \rightarrow H^\bullet + H_2O$	$2.16 \times 10^8$	1.51	3.43
$OH^\bullet + OH^\bullet \rightarrow O^\bullet + H_2O$	$3.57 \times 10^4$	2.40	-2.11
$H^\bullet + H^\bullet (+M) \rightarrow H_2 (+M)$	$1.00 \times 10^{18}$	-1	
$H^\bullet + OH^\bullet (+M) \rightarrow H_2O (+M)$	$2.20 \times 10^{22}$	-2	
$O^\bullet + H^\bullet (+M) \rightarrow OH^\bullet (+M)$	$5.00 \times 10^{17}$	-1	
$O^\bullet + O^\bullet (+M) \rightarrow O_2 (+M)$	$1.20 \times 10^{17}$	-1	
$H^\bullet + O_2 (+M) \rightarrow OOH^\bullet (+M)$	$2.80 \times 10^{18}$	-0.86	
$OH^\bullet + OH^\bullet (+M) \rightarrow H_2O_2 (+M)$	$7.40 \times 10^{13}$	-0.37	
$OOH^\bullet + H^\bullet \rightarrow H_2O + O^\bullet$	$3.97 \times 10^{12}$		0.671
$H_2O + O^\bullet \rightarrow O_2 + H_2$	$2.80 \times 10^{13}$		1.068
$OOH^\bullet + H^\bullet \rightarrow OH^\bullet + OH^\bullet$	$1.34 \times 10^{14}$		0.635
$OOH^\bullet + O^\bullet \rightarrow OH^\bullet + O_2$	$2.00 \times 10^{13}$		
$OOH^\bullet + OH^\bullet \rightarrow O_2 + H_2O$	$2.90 \times 10^{13}$		-0.5
$OOH^\bullet + OOH^\bullet \rightarrow O_2 + H_2O_2$	$1.30 \times 10^{11}$		-1.63
$H_2O_2 + H^\bullet \rightarrow H_2 + OOH^\bullet$	$1.21 \times 10^7$	2	5.2
$H_2O_2 + H^\bullet \rightarrow H_2 + O + OH^\bullet$	$1.00 \times 10^{13}$		3.6
$H_2O_2 + O^\bullet \rightarrow OH^\bullet + OOH^\bullet$	$9.63 \times 10^6$	2	4.0
$H_2O_2 + OH^\bullet \rightarrow H_2O + OOH^\bullet$	$1.75 \times 10^{12}$	2	0.32

Note: M is any inert molecule.

As shown in Table 7.8.1, there are about 20 possible reactions when the list is limited to only the species containing oxygen and hydrogen (not considering inert molecules M). Many other reactions should be included in a complete list of possibilities. The free radicals such as  $\text{H}^\bullet$ ,  $\text{OH}^\bullet$ ,  $\text{OOH}^\bullet$ , and  $\text{O}^{\bullet\bullet}$  further interact with the fuel molecules producing by propagation a multitude of other reactions. When computer programs are used for the simulation of burning, hundreds of model reactions and numerous molecular species are included even for single compound flames such as acetylene, ethylene, hexane, and benzene. The models become even more complicated when considering fuel mixtures or several types of flames (premixed, lean or rich in fuel, etc.). The model reactions allow the prediction of flame composition and PAH formation [22,155, 192,319,320]. Soot structure [304,312,321–324], influence of solid surfaces in soot and PAH formation [325], and other aspects of PAHs and soot formation in flames were also subjects of computer modeling.

Not only the formation of PAHs in flames has been studied, but also their potential oxidation with the formation of furans and other oxygenated rings (pyrans and dioxins). These transformations in flames are important for the understanding of the formation of chlorinated dioxins when sources of covalently bound chlorine are available [326,327].

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## CHAPTER 8

*Pyrolysis of Halogenated Hydrocarbons***8.1. CHLORINATED ALIPHATIC HYDROCARBONS*****General aspects***

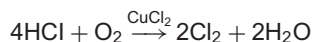
The replacement in a hydrocarbon of one or more hydrogen atoms with chlorine atoms leads to the class of chlorinated hydrocarbons. This replacement can be performed on any kind of hydrocarbon, including linear, branched, or cyclic, saturated or unsaturated, as well as aromatic. Chlorinated hydrocarbons are also known as chlorocarbons and can be viewed as formed from an organic radical (alkyl, cycloalkyl, aryl, etc.) and one or more chlorine functional groups. In chlorinated aliphatic hydrocarbons, the chlorine atoms are attached to an aliphatic structure. The compounds such as benzyl chloride, where, besides chlorine, the aliphatic structure is substituted with an aryl group, are still considered aliphatic.

For a single hydrocarbon, there are many possibilities for hydrogen replacements. For propane, for example, there are 29 possible chlorinated derivatives, for *n*-hexane there are 666, and for *n*-heptane there are 1998. A large number of all the possible chlorinated compounds have not been individually prepared and do not have a particular application. However, some chlorinated hydrocarbons are important industrial and consumer products. Among these are compounds used as intermediates in industrial organic synthesis, chlorinated monomers used in polymer industry such as vinyl chloride and 1,1-dichloroethylene, and chlorinated solvents such as tetrachloroethylene, 1,2-dichloroethane, methylene chloride, and chloroform.

A variety of other uses can be found for chlorinated compounds. These include pesticides and herbicides (common examples being lindane, mirex, and aldrin), disinfectants, flame retardants (e.g., Dechlorane Plus), and pharmaceuticals. However, most of these compounds have more complex structures including, besides chlorine, other molecular structures (e.g., heterocycles), as well as additional functional groups such as OH, NH<sub>2</sub>, COOH, F, Br, and I. Pyrolysis of compounds with multiple functional groups will be discussed in other chapters of this book.

The study of pyrolysis of chlorinated hydrocarbons (and of chlorinated compounds in general) is important in relation to health and environmental issues. Industrial incineration is a common procedure for reducing the original volume of various types of waste. Due to the presence of chlorinated compounds in waste, incinerators are a major source of chlorinated pollutants. This includes small molecules such as vinyl chloride and larger aromatic molecules such as (poly)chlorinated dibenzo-*p*-dioxins (commonly referred to as dioxins or PCDD, for simplicity), (poly)chlorinated dibenzofurans (sometimes referred to as furans or PCDF), and (poly)chlorinated biphenyls (PCBs). PCDDs, PCDFs, and PCBs are also known as "dioxin-like compounds" or DLC. Vinyl chloride (which is toxic and carcinogenic) is also generated by pyrolysis from other chlorinated molecules [1,2] and from polymers such as polyvinyl chloride (see e.g., [3]). Of particular interest is the generation of dioxins, furans, and PCBs. Some of these compounds are carcinogens, highly toxic substances, and persistent pollutants with high propensity for bioaccumulation. The main sources of dioxins and furans are related to the pyrolysis of chlorophenols and other similar compounds. However, the formation of PCBs, dioxins, and furans also may take place at low levels from the pyrolysis or oxidative pyrolysis of certain chlorinated aliphatic hydrocarbons [4–6]. The generation of dioxins and furans from chlorinated organic compounds in industrial incinerators [7,8] and from other burning processes is of considerable concern and has been the subject of numerous studies [9–11]. There are two temperature windows in which DLCs can form, the homogeneous route between 500 °C and 800 °C and the heterogeneous route that involves temperatures as low as 200–400 °C. Homogeneous reactions are the result of the pyrolytic rearrangement in the gas phase of chlorinated precursors such as chlorinated cycloalkanes, chlorobenzenes, and especially chlorophenols. Heterogeneous formations are catalyzed reactions

that take place on the ash or soot particles present in combustion systems. The “de novo” reactions are also possible, and they involve the oxidation and chlorination of any unburned organic compound and carbon particles. The formation of free halogens may occur from organic and inorganic sources by reactions taking place under the influence of heat. For example, in many pyrolytic reactions the decomposition takes place with the generation of HCl. This compound reacting with oxygen in flames (particularly in the presence of catalysts such as CuO/CuCl<sub>2</sub>) produces chlorine:



The free chlorine (or bromine) generated in this type of reaction can react further with nonhalogenated molecules and can form undesirable halogenated compounds that initially were not a result of pyrolysis. Thermal decomposition of HCl also may result in the formation of Cl<sup>•</sup> free radicals. This process may occur, for example, during reaction of HCl with OH<sup>•</sup> free radicals. The reaction of various organic species with Cl<sup>•</sup> free radicals is another potential path for the generation of halogenated compounds from nonhalogenated molecules. In this way, the final pyrolysate, particularly of complex mixtures such as various types of waste, may contain harmful halogenated compounds.

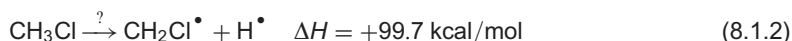
The exposure to chlorinated dibenzo-*p*-dioxins, chlorinated dibenzofurans, and chlorinated biphenyls typically occurs from a complex mixture of these compounds and not from individual species. For this reason, a toxic equivalency factor (TEF) has been developed as a tool to assess the health risk for individual DLCs in a mixture. Toxicity of PCBs is discussed further in Section 24.1. Chlorinated dibenzo-*p*-dioxins can be classified chemically as chlorinated ethers, while chlorinated dibenzofurans as derivatives of oxygenated aromatic heterocycles. Additional information on these compounds is found in Chapters 9, 21 and 24. Pyrolysis results for several individual chlorinated aliphatic hydrocarbons are further discussed below.

### Chlorinated derivatives of methane

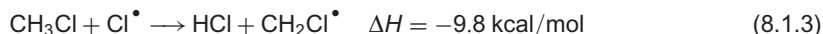
Methane can form four chlorinated derivatives, including chloromethane, dichloro-methane (methylene chloride), trichloromethane (chloroform), and tetrachloromethane (carbon tetrachloride). The pyrolysis process of chlorinated derivatives of methane follows a path similar to that of methane, with the decomposition temperatures somewhat lower than that of methane itself. This is expected, considering that the bond strength for C–Cl is about 20 kcal/mol weaker than the C–H bond. For example, the bond strength for CH<sub>3</sub>–H is 104.3 kcal/mol, while for CH<sub>3</sub>–Cl it is 84.1 kcal/mol; the bond strength for CCl<sub>3</sub>–H is 96.1 kcal/mol, while for CCl<sub>3</sub>–Cl is 73.1 kcal/mol. Pyrolysis of CH<sub>3</sub>Cl begins around 450 °C. The first step is the formation of methyl radicals and chlorine atoms:



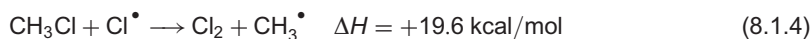
The formation of a hydrogen atom and CH<sub>2</sub>Cl<sup>•</sup> free radical involving a C–H bond cleavage is more endothermic with a energy difference of 16.4 kcal/mol and not a likely initiation step:



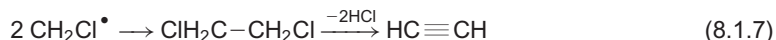
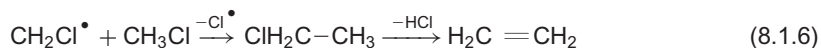
The initiation reaction is followed by propagation steps and by secondary reactions. Formation of HCl results from reactions of the type:



The formation of HCl in reaction 8.1.3 is an exothermic process (at 25 °C) and dominates the pyrolysis, while the potential formation of chlorine molecules and of CH<sub>3</sub><sup>•</sup> radical is an endothermic reaction and therefore not favored:



This explains why the main reaction products of  $\text{CH}_3\text{Cl}$  pyrolysis are  $\text{HCl}$  and various hydrocarbons [12] including  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ , etc. In addition to  $\text{HCl}$  and hydrocarbons, soot is formed as the reaction time increases. The hydrocarbons seen in  $\text{CH}_3\text{Cl}$  pyrolysate are formed in reactions of the types shown below:



Other similar reactions lead to the formation of ethane, chloroethane, vinyl chloride, etc., which are detected in traces in the  $\text{CH}_3\text{Cl}$  pyrolysate [13]. Kinetic parameters regarding these reactions have been reported in the literature [14]. The distribution of the main hydrocarbons formed during pyrolysis of  $\text{CH}_3\text{Cl}$  in a shock tube experiment for a reaction time of about 0.5 s at various temperatures for a mixture of 3% (vol.)  $\text{CH}_3\text{Cl}$  vapors diluted with 10%  $\text{N}_2$  and argon [15] is shown in Figure 8.1.1.

Soot also is formed in the pyrolysate of  $\text{CH}_3\text{Cl}$ . The formation of  $\text{C}_2\text{H}_2$  from  $\text{CH}_3\text{Cl}$  further leads to the formation of aromatic rings through condensations similar to those discussed for the pyrolysis of hydrocarbons (see Chapter 7).

Pyrolysis of  $\text{CH}_2\text{Cl}_2$  is similar to that of  $\text{CH}_3\text{Cl}$ , but the content of chlorinated compounds formed in addition to hydrocarbons is slightly higher. In addition, the sooting tendency of  $\text{CH}_2\text{Cl}_2$  is higher compared to that of  $\text{CH}_3\text{Cl}$ . The reactions taking place during  $\text{CH}_2\text{Cl}_2$  pyrolysis starts with the generation of various radicals as shown below:



Further reactions will take place involving these radicals, and the increase in the number of carbons from termination reactions is a likely process:

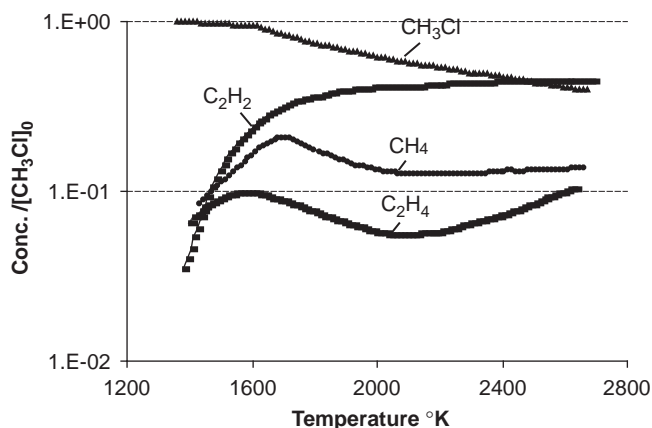


FIGURE 8.1.1. Distribution of the main products formed during pyrolysis of  $\text{CH}_3\text{Cl}$  in a shock tube experiment (smooth interpolation fit of experimental data) [15].

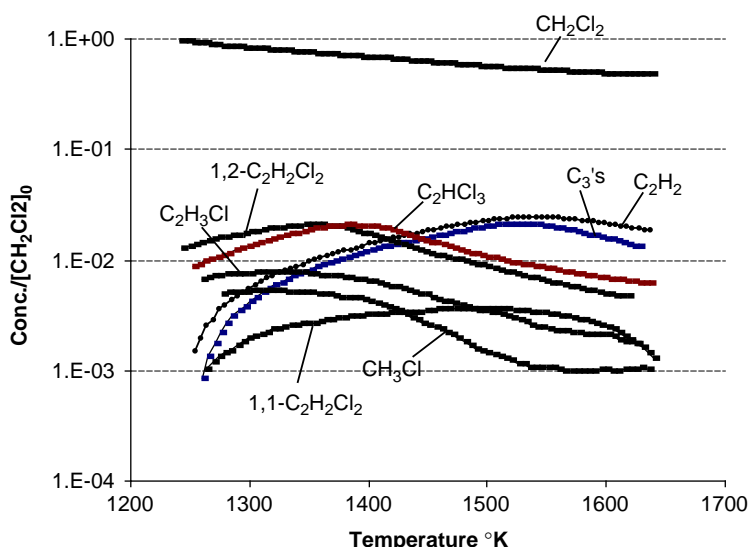
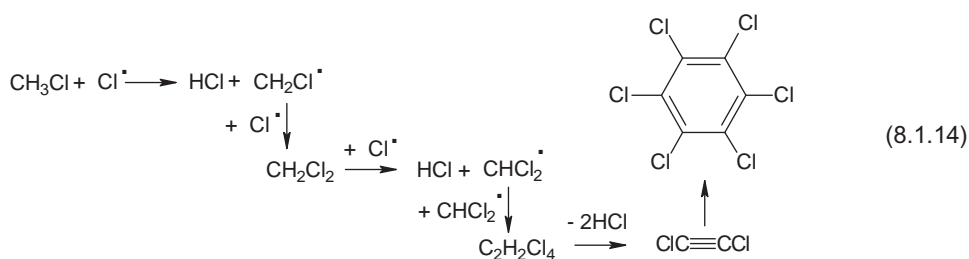


FIGURE 8.1.2. Distribution of the main products formed during pyrolysis of  $\text{CH}_2\text{Cl}_2$  in a shock tube experiment (smooth interpolation fit of experimental data) [15].

The resulting  $\text{C}_2$  chlorinated compounds easily eliminate  $\text{HCl}$  and form unsaturated hydrocarbons, continuing with condensation reactions similar to those described for hydrocarbons. The distribution of pyrolysis products of  $\text{CH}_2\text{Cl}_2$  in a shock tube experiment for a reaction time of about 0.5 s at various temperatures of 3% (vol.)  $\text{CH}_2\text{Cl}_2$  vapors diluted with 10%  $\text{N}_2$  and argon [15] is shown in Figure 8.1.2.

The pyrolysis of chlorinated methane derivatives also has the potential to generate traces of thermally stable hexachlorobenzene ( $\text{cyc-C}_6\text{Cl}_6$ ). The formation of  $\text{cyc-C}_6\text{Cl}_6$  from  $\text{CH}_3\text{Cl}$  [13] or  $\text{CH}_2\text{Cl}_2$  [16] depends exclusively on complex secondary reactions, which are not favored during pyrolysis. One potential path of formation of chlorinated aromatic compounds goes through dichloroethyne (dichloroacetylene), which further forms  $\text{cyc-C}_6\text{Cl}_6$ . This path is based on the sequence of reactions of the type:

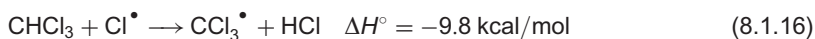


As shown in the reaction sequence 8.1.14, only some termination reactions may lead to the increase in the number of chlorine atoms per carbon, and for this reason the yield of chlorinated aromatics from  $\text{CH}_3\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  is low. On the other hand, when starting with higher chlorination of the initial compound ( $\text{CHCl}_3$  and  $\text{CCl}_4$ ), the yield of  $\text{cyc-C}_6\text{Cl}_6$  increases.

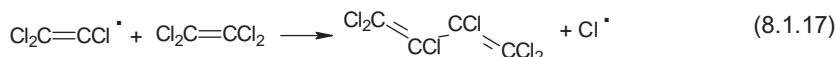
The initial steps in  $\text{CHCl}_3$  pyrolysis follow the same rules as for  $\text{CH}_3\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  (the cleavage of  $\text{C-H}$  bond is less likely compared to the cleavage of  $\text{C-Cl}$  bond):



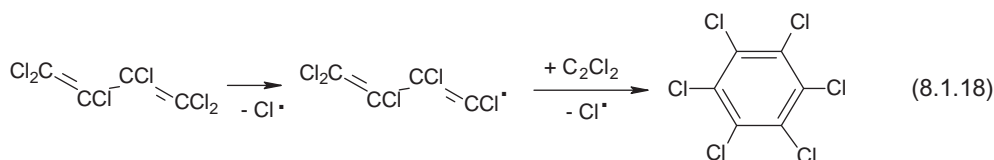
The initial reaction is followed by secondary reactions of the type:



Once the hydrogen atoms are captured as HCl, a multitude of other reactions may occur involving the excess of chlorinated radicals. Similar to the formation of ethane, ethylene, and acetylene from methane,  $\text{CCl}_3^\bullet$  radicals may react leading to the formation of molecules such as  $\text{C}_2\text{Cl}_6$ ,  $\text{C}_2\text{Cl}_4$ , and  $\text{C}_2\text{Cl}_2$ . Continuation of heating leads to formation of carbon and small amounts of aromatic compounds. The mechanisms of formation of chlorinated aromatic hydrocarbons seem to be favored by the capability of chlorinated radicals to undergo reversible additions followed by elimination of smaller radicals. Tetrachloroethylene formed as an intermediate compound from chlorinated radicals may lead to 1,3-hexachlorobutadiene in a reaction of the type:



1,3-Hexachlorobutadiene may react in Diels–Alder type condensations (or radicalic condensation) followed by  $\text{Cl}_2$  elimination to form  $\text{cyc-C}_6\text{Cl}_6$ . Alternative paths involve radical mechanisms of the type:



The formation of  $\text{cyc-C}_6\text{Cl}_6$  can be associated with the formation of PCBs.

Pyrolysis in the presence of oxygen increases the potential formation of  $\text{cyc-C}_6\text{Cl}_6$ , since some of the hydrogen atoms present in a chlorinated hydrocarbon have the chance to form  $\text{H}_2\text{O}$  and not HCl, leaving a higher proportion of chlorine bound to carbon in the pyrolysis products. This observation was investigated in detail for the development of reductive pyrolysis processes, which increases the yield of HCl on the account of chlorinated aromatics (PCBs) [17]. The product distribution from the atmospheric pressure oxidative pyrolysis of  $\text{CHCl}_3$  is shown in Figure 8.1.3 [12]. The process took place in a fuel/oxygen equivalence ratio 3:1 with  $\text{CHCl}_3$  initial molar concentration  $2.7 \times 10^{-5}$  mol/L at a pressure of 1.15 atm and an exposure time of 2 s.

As shown in Figure 8.1.3, measurable amounts of  $\text{cyc-C}_6\text{Cl}_6$  are formed in  $\text{CHCl}_3$  oxidative pyrolysis. Reductive pyrolysis, which generates lower levels of chlorinated hydrocarbons and more HCl, has been evaluated frequently for the destruction of chlorinated hazardous waste and is described in numerous reports [18,19].

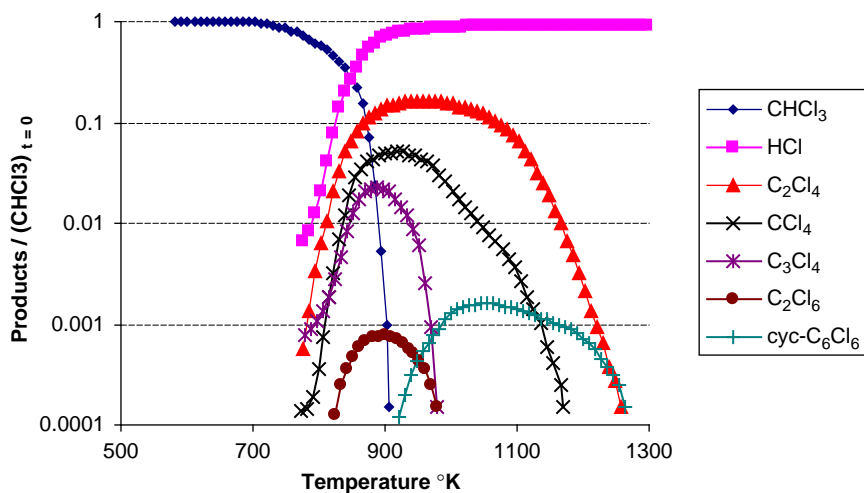
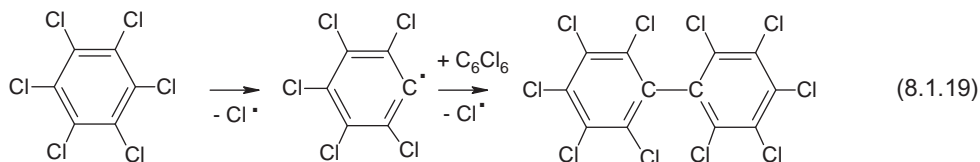


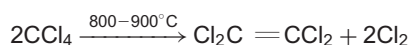
FIGURE 8.1.3. Product distribution from the atmospheric pressure oxidative pyrolysis of  $\text{CHCl}_3$  (smooth interpolation fit of experimental data) [12].

The formation of cyc-C<sub>6</sub>H<sub>6</sub> in reaction 8.1.18 can be continued with the formation of chlorinated biphenyls. Similar to the formation of biphenyl from benzene, under the influence of heat the following reaction may occur:



Reaction 8.1.19 shows the generation of a perchlorobiphenyl, but the toxicity of PCBs ranked using the TEFs shows that the maximum TEF is obtained for PCBs that do not have all hydrogens replaced with chlorine. The generation of compounds with some chlorine and some hydrogen substituents to the biphenyl ring is also possible by the pyrolysis of chlorinated aliphatic hydrocarbons.

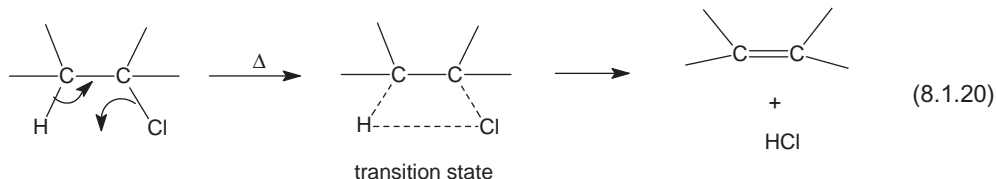
Pyrolysis of CCl<sub>4</sub> does not generate HCl, since no hydrogen is available in the molecule. At temperatures 800–900 °C, CCl<sub>4</sub> generates tetrachloroethylene:



An important process in thermal decomposition of CH<sub>3</sub>Cl and CH<sub>2</sub>Cl<sub>2</sub> is the formation of HCl and unsaturated hydrocarbons. These hydrocarbons further undergo condensations to form heavier molecules and soot, following a process closer to that encountered for hydrocarbons (although with a faster kinetics due to the presence of the initial chlorine substitutions). Soot formation from chlorinated hydrocarbons is an undesirable process, being associated with formation of PAHs and PCBs. The generation of soot and heavier compounds involving hydrocarbons (leading to PAHs) takes place only partially for the case of CHCl<sub>3</sub>, perchlorinated intermediaries also contributing to the soot formation. In the case of CCl<sub>4</sub>, only chlorinated molecules are involved in soot formation. The radicalic mechanism in CCl<sub>4</sub> pyrolysis resembles that of methane. Soot formation from CCl<sub>4</sub> takes place at a higher temperature than that from CH<sub>3</sub>Cl [15]. The sooting tendency of CCl<sub>4</sub> is seven times higher than that of CH<sub>4</sub> when pyrolyzed at 1623 K [20]. Results on pyrolysis of CCl<sub>4</sub> in the presence of CH<sub>4</sub> have been reported as well [15]. In this pyrolysis reaction, free chlorine atoms compete for the hydrogen atoms on methane, generating HCl. More detailed kinetic parameters for the thermal decomposition of the chlorinated derivatives of methane are reported in the literature (see e.g., [21]).

### Chlorinated derivatives of other small hydrocarbons

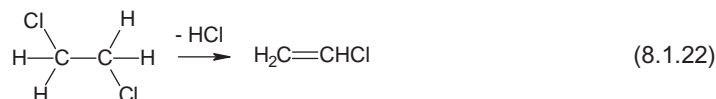
Pyrolysis of chlorinated hydrocarbons with two or more carbons that also contain some hydrogens in the molecule may be initiated by the cleavage of a C–Cl bond similar to those noticed for chlorinated derivatives of methane, but a β-elimination (see Section 2.2) with a concerted mechanism is also a common reaction. This elimination leads to the formation of HCl and of a double bond in the parent molecule, as shown below:



Chloroethane, for example, heated at 510–530 °C generates ethene (with a 55.4% yield) and HCl by the following reaction:

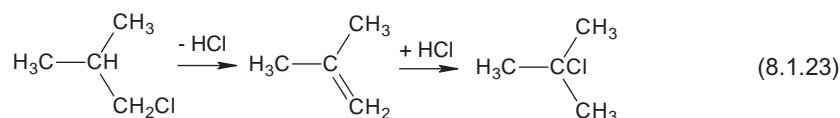


The reaction can be catalyzed with  $\text{BaCl}_2$ , and at about  $450^\circ\text{C}$ , the yield of ethylene from chloroethane is close to 100%. Similarly, propylene is quantitatively generated from chloropropane. In the presence  $\text{BaCl}_2$  as a catalyst, dichloroethane generates vinyl chloride at a temperature as low as  $250^\circ\text{C}$  in a reaction as shown below:



In the absence of the catalyst, the reaction of formation of vinyl chloride starts around  $300^\circ\text{C}$ . The low temperature necessary for these reactions indicates a concerted mechanism rather than one involving free radicals. This reaction has industrial applications.

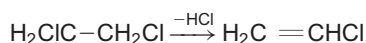
The elimination of  $\text{HCl}$  from chlorinated hydrocarbons containing hydrogen atoms in the molecule seems to be a reversible reaction since the alkene may react back with the generated acid. This process is illustrated in the pyrolysis of 1-chloro-2-methylpropane by the formation of some 2-chloro-2-methylpropane in the pyrolysate. The  $\text{HCl}$  reacts back with the alkene following Markovnikov's rule (halogen becomes attached to the carbon with the fewest hydrogens) in a sequence of reactions as follows:



This type of isomerization, with the migration of the halogen from a less substituted to a more substituted carbon, is typical for halogenated compounds and takes place at different temperatures in the range of  $200\text{--}250^\circ\text{C}$ , depending on the nature of the compound and the heating time (see e.g., [22]).

Among other chlorinated hydrocarbons for which pyrolysis or oxidative pyrolysis results were reported are 1,2-dichloroethane, trichloroethene [12,23], tetrachloroethane [24], hexachlorobutadiene [25], and hexachloropropene [26].

Pyrolysis of 1,2-dichloroethane ( $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ ) is an important technological process for the fabrication of vinyl chloride. The reaction occurs around  $480^\circ\text{C}$  as shown below:

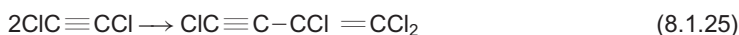


In addition to vinyl chloride, the reaction generates traces of other chlorinated compounds and of butadiene [27]. Further heating at higher temperatures compared to that of 1,2-dichloroethane decomposition leads to the formation of acetylene and PAHs from further elimination of  $\text{HCl}$  and condensation reactions.

Pyrolysis of trichloroethene ( $\text{C}_2\text{HCl}_3$ , trichloroethylene) (heat of formation  $\Delta H_f^\circ = -4.2 \text{ kcal/mol}$ ) has been evaluated in the temperature range  $573\text{--}1273 \text{ K}$  [12,23]. At lower temperatures the formation of  $\text{HCl}$  probably takes place by a concerted mechanism similar to reaction (8.1.20) with the formation of dichloroacetylene ( $\text{C}_2\text{Cl}_2$ ).



Dimerization of dichloroacetylene generates 1,1,2,4-tetrachlorobut-1-en-3-yne ( $\text{C}_4\text{Cl}_4$ ), which is a major product of pyrolysis of  $\text{C}_2\text{HCl}_3$ . This dimerization reaction is shown below:



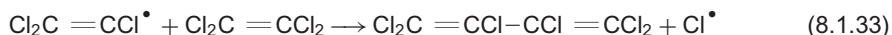
Above  $1000 \text{ K}$ , the main result of the pyrolysis process is the formation of  $\text{C}_2\text{Cl}_4$ ,  $\text{C}_4\text{Cl}_4$ , and  $\text{cyc-C}_6\text{Cl}_6$ . The formation of these compounds may involve a radicalic mechanism. The process can start



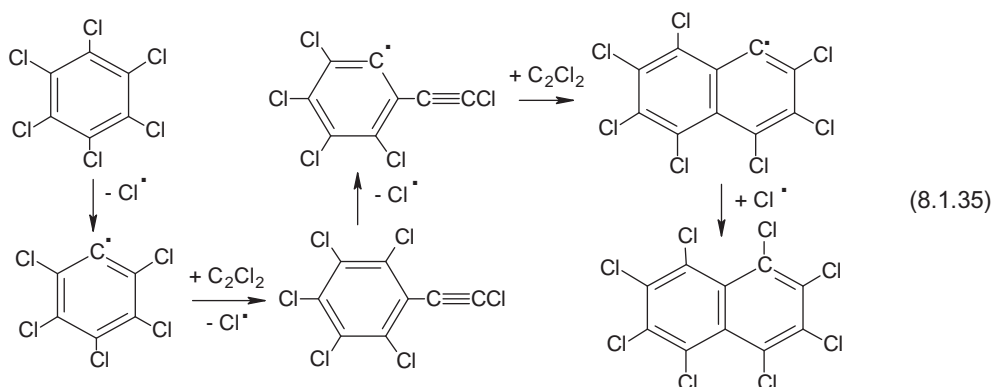
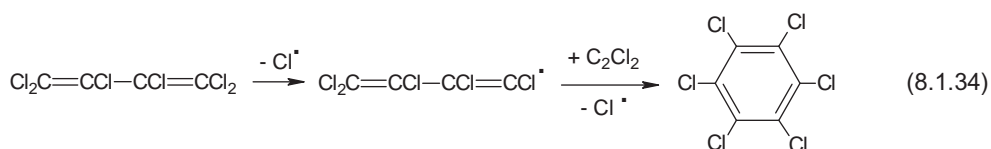
$$\begin{array}{lcl} \text{ClHC}=\text{CCl}_2 & \begin{array}{l} \nearrow \\ \searrow \end{array} & \begin{array}{l} \text{HC}=\text{CCl}_2 + \text{Cl}^\cdot \quad \Delta H^\circ = +86.0 \text{ kcal/mol} \\ \text{ClHC}=\text{CCl}^\cdot + \text{Cl}^\cdot \quad \Delta H^\circ = +77.8 \text{ kcal/mol} \end{array} \end{array} \quad (8.1.26)$$
$$\text{C}_2\text{HCl}_3 + \text{Cl}^\bullet \longrightarrow \text{C}_2\text{Cl}_3^\bullet + \text{HCl} \quad (8.1.27)$$
$$\text{C}_2\text{Cl}_3^\bullet + \text{Cl}^\bullet \longrightarrow \text{C}_2\text{Cl}_4 \quad (8.1.28)$$
$$\text{ClHC}=\text{CCl}^{\bullet} + \text{Cl}^{\bullet} \rightarrow \text{HCl} + \text{ClC}\equiv\text{CCl} \quad (8.1.29)$$
$$\text{C}_2\text{Cl}_3^\bullet + \text{C}_2\text{Cl}_2 \longrightarrow \text{C}_4\text{Cl}_4 + \text{Cl}^\bullet \quad (8.1.30)$$
[illegible]
$$\text{C}_2\text{Cl}_4 \longrightarrow \text{C}_2\text{Cl}_3^\bullet + \text{Cl}^\bullet \quad \Delta H^\circ = +80.2 \text{ kcal/mol} \quad (8.1.32)$$

Above 1100 K, molecular growth starts to form chlorinated compounds with four, six, etc. carbon atoms. Chlorine atoms further react with  $C_2Cl_4$  with formation of  $Cl_2$  and more  $C_2Cl_3^{\cdot}$  free radicals and do not generate  $C_2Cl_5^{\cdot}$ , as proven by the lack of formation of  $CCl_4$  and  $C_2Cl_6$ . The  $C_2Cl_3^{\cdot}$  free radicals can lose a  $Cl^{\cdot}$  atom to form  $C_2Cl_2$  or can react with  $Cl_2$  to form  $Cl^{\cdot}$  and re-form  $C_2Cl_4$ . Also common are

propagation reactions of the type:



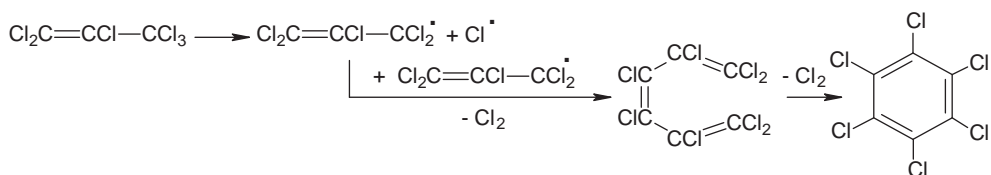
The formation of cyc-C<sub>6</sub>Cl<sub>6</sub> and heavier chlorinated compounds can follow the formation of hexachloro-1,3-butadiene. This compound and C<sub>2</sub>Cl<sub>2</sub> can be the source of heavier chlorinated aromatic hydrocarbons found in the pyrolysates of a number of chlorinated aliphatic hydrocarbons. Examples of paths for cyc-C<sub>6</sub>Cl<sub>6</sub> and further cyc-C<sub>10</sub>Cl<sub>8</sub> formation are given below:



The free radical C<sub>4</sub>Cl<sub>5</sub><sup>•</sup> can be stabilized by resonance, although the more stable form of the radical seems to be less involved in the molecular growth during pyrolysis.

Pyrolysis of C<sub>2</sub>Cl<sub>4</sub> was studied also in the presence of H<sub>2</sub> (diluted with argon in the ratio C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>/Ar = 0.5/7.0/92.5) [28]. Pyrolysis of C<sub>2</sub>Cl<sub>4</sub> in the presence of H<sub>2</sub> leads to the formation of HCl, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and chlorinated compounds such as CH<sub>3</sub>Cl, CH<sub>2</sub>CCl<sub>2</sub>, C<sub>2</sub>HCl<sub>3</sub>. Traces of other compounds including C<sub>1</sub> to C<sub>4</sub> hydrocarbons, benzene, toluene, styrene, and chlorinated compounds such as CHCl=CHCl, C<sub>2</sub>Cl<sub>2</sub>, C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)Cl, C<sub>6</sub>H<sub>5</sub>Cl, and C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> also were detected in the pyrolysate. The study was focused on the determination of reaction paths and kinetic parameters, showing the possibility of using hydrogen during the pyrolysis/combustion of chlorinated compounds to convert chlorocarbons into HCl and hydrocarbons instead of into PCBs. The reported modeling of the process [28] used 183 potential reactions with established rate constants. The formation of partially chlorinated PCBs during pyrolysis in the presence of hydrogen is a potential negative aspect of this procedure, since perchlorinated PCBs have a lower TEF as compared to the PCBs with hydrogen atoms in *ortho* positions.

Similarly to the other perchlorinated hydrocarbons, hexachloropropene (C<sub>3</sub>Cl<sub>6</sub>) starts decomposing with a C–Cl bond scission [25]. The initial decomposition products include C<sub>2</sub>Cl<sub>4</sub> and C<sub>3</sub>Cl<sub>4</sub>. The formation of larger molecules starts to be noticed around 800 K, mainly with the formation of cyc-C<sub>6</sub>Cl<sub>6</sub>. Several paths are possible for the formation of cyc-C<sub>6</sub>Cl<sub>6</sub>, one of these paths being the termination reaction between two C<sub>3</sub>Cl<sub>5</sub><sup>•</sup> radicals:

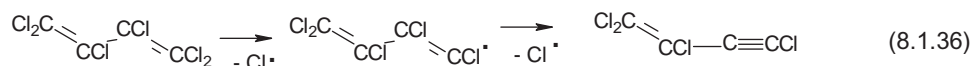


Other paths involve the formation of  $C_3Cl_3^{\bullet}$  radicals and their recombination or involve reactions between chlorinated  $C_2$  and  $C_4$  pyrolysis products.

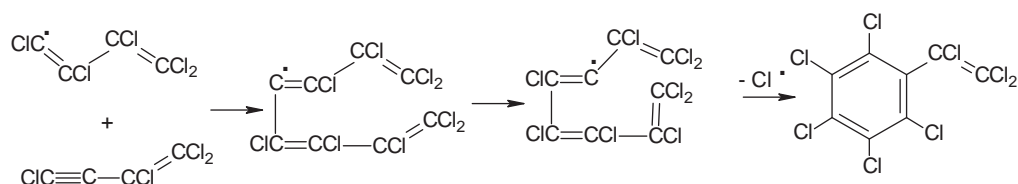
Pyrolysis of hexachlorobutadiene ( $C_4Cl_6$ ) starts with an initiation described by the first part of reaction 8.1.18 leading to  $Cl^{\bullet}$  atoms and  $C_4Cl_5^{\bullet}$  radicals. The  $Cl^{\bullet}$  atoms are able to react with one of the double bonds of  $C_4Cl_6$  as follows:



This reaction explains the formation of  $C_2Cl_4$  as a major thermal decomposition product of  $C_4Cl_6$ . The free radicals  $C_4Cl_5^{\bullet}$  may decompose further to generate  $Cl^{\bullet}$  and 1,1,2,4-tetrachlorobut-1-en-3-yne ( $C_4Cl_4$ ), which is another major pyrolysis product of  $C_4Cl_6$ :



A different path for consumption of  $C_4Cl_5^{\bullet}$  radicals, due to the presence of  $C_2Cl_2$ , is shown in reaction 8.1.18. Reaction 8.1.36 takes place by a  $\beta$ -scission of a C–Cl bond in the free radical. Another path of  $C_4Cl_5^{\bullet}$  radical's consumption is the reaction with  $C_4Cl_4$  and the formation of  $C_8Cl_9^{\bullet}$  followed by an intramolecular Cl abstraction and the formation of octachloro ethenylbenzene:



Reaction 8.1.18 is possible also for hexachlorobutadiene, when  $C_2Cl_2$  starts to be present in the pyrolysate as a result of reactions of the type:



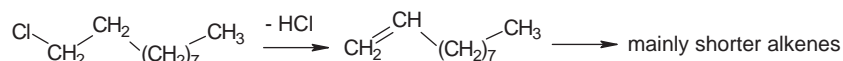
The formation of larger compounds starts above 1050 K [25]. A detailed reaction kinetic model involving 20 elementary reactions for the formation of larger molecules up to  $C_{12}$  is described in the literature [12].

Pyrolysis of chlorinated hydrocarbons as it takes place in industrial incinerators was found to be a source of chlorinated dioxins, furans, and PCBs. Pyrolysis of model compounds in the absence of oxygen, as previously discussed, does not fully explain the amount of undesirable compounds generated in these incinerators [29]. The participation of oxygen with the formation of phenols and chlorinated phenols may play an important role in DLC formation, since the chlorophenols pyrolysis is a likely source of DLCs. Also, the reaction of HCl with unsaturated hydrocarbons (acetylene, butadiene, etc.), all formed during pyrolysis, may lead to precursors that further generate partially chlorinated biphenyls, chlorinated dioxins, and chlorinated dibenzofurans. Chlorine generated in some decomposition reactions may be involved in “de novo” pathways of DLC formation by reacting with organic components and forming various chlorinated compounds. These processes are influenced by the presence of solid particles, mainly of carbon but also of  $SiO_2$ ,  $Al_2O_3$ , and specific metal oxides such as CuO [30,31]. Continuous effort is made to reduce the formation of DLCs during the pyrolysis of halogenated compounds by using catalysts, reducing conditions (hydrogen), or steam [32]. Further information on DLC formation can be found in Section 8.3.

### Other chlorinated derivatives of aliphatic hydrocarbons

Chlorinated aliphatic hydrocarbons are relatively common compounds, and only a very limited number of them are discussed here. However, the general behavior during pyrolysis is similar for the

whole class of compounds. When hydrogen atoms are present in the molecule, HCl is eliminated, typically by a reaction similar to 8.1.20. Intermediate compounds that are perchlorinated (no hydrogen available) or parent compounds with no hydrogen in the molecule undergo pyrolysis by a radicalic mechanism with a C–Cl bond cleavage. A radicalic mechanism is more likely to occur when pyrolysis is performed at high temperatures (above 900–1000 °C). Chlorinated hydrocarbons with a long aliphatic chain and a few chlorine atoms generate alkenes that further decompose as previously discussed in Section 7.3. This type of reaction is exemplified below for 1-chlorodecane:



A pyrogram for 1-chlorodecane is shown in Figure 8.1.4. The experiment was performed on 0.25 mg compound using Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900\text{ °C}$ ,  $\beta = 10\text{ °C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280\text{ °C}$ . The pyrolysate was analyzed by GC/MS under conditions given in Table 4.6.1. The compound identifications in the pyrogram and their relative molar content in 100 moles of pyrolysate are given in Table 8.1.1. The calculation of the mole percent was obtained based solely on peak areas, and since differences in the MS response factors can be quite large, the estimations may have large errors.

As shown in Figure 8.1.4 and Table 8.1.1, the pyrolysate consists of a relatively complex mixture. Besides undecomposed 1-chlorodecane (due to evaporation before the sample reached the decomposition temperature), 1-decene is the main pyrolysis product. Some back-reaction of HCl with various alkenes to form chlorinated alkanes is a likely side reaction. Also, the decomposition of the hydrocarbon chain by radicalic mechanism and the formation of  $\omega$ -chloro-1-alkenes seem to be another secondary reaction path. Radicalic processes with the cleavage of a C–C bond in the hydrocarbon chain probably occurred, although not as the main pyrolysis mechanism. The fragment alkenes are sometimes associated, as expected, with low levels of alkadienes. Some aromatic hydrocarbons such as benzene and toluene are also present in the pyrolysate. The decomposition reactions depend on pyrolysis conditions (temperatures, heating time, etc.) and may not be identical for some other chlorinated compounds.

Compounds with higher levels of chlorination and also containing hydrogen atoms will form compounds with multiple double bonds and further have a higher propensity to form partly chlorinated aromatic hydrocarbons. As an example, the pyrogram of  $\gamma$ -1,2,3,4,5,6-hexachlorocyclohexane (eeeeaa;)

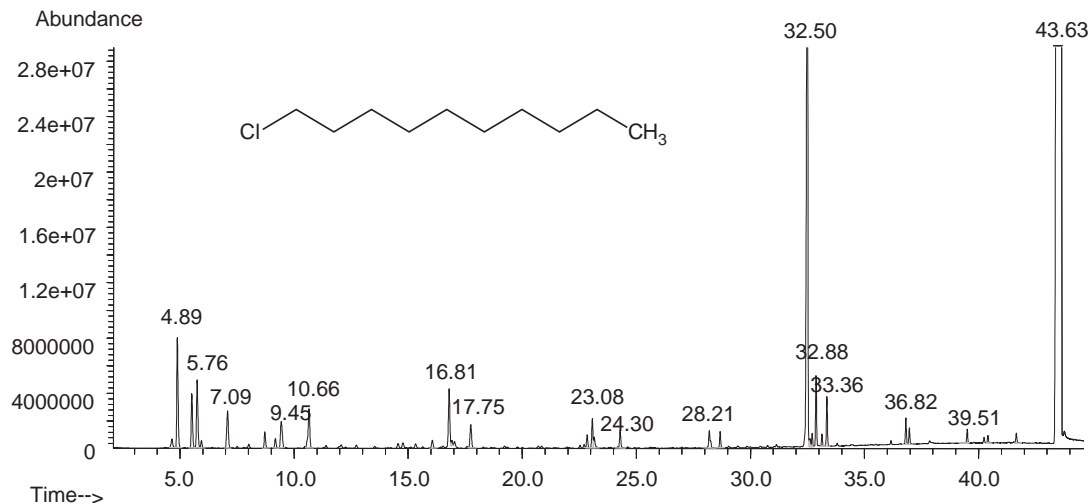


FIGURE 8.1.4. Pyrogram of 1-chlorodecane at 900 °C. Peak assignment is given in Table 8.1.1.

TABLE 8.1.1. Identification of the main peaks in the chromatogram shown in Figure 8.1.4 for the pyrolysis of 1-chlorodecane

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Propene	4.89	42	115-07-1	7.52
2	1-Butene	5.53	56	106-98-9	2.80
3	1,3-Butadiene	5.76	54	106-99-0	3.84
4	2-Butene	5.95	56	107-01-7	0.38
5	1-Pentene	7.09	70	109-67-1	1.90
6	1,3-Pentadiene	8.73	68	504-60-9	0.72
7	1,4-Pentadiene	9.19	68	591-93-5	0.44
8	Cyclopentadiene	9.45	66	542-92-7	1.57
9	1-Hexene	10.66	84	592-41-6	1.78
10	Methylcyclopentane	12.76	84	96-37-7	0.09
11	1-Methylcyclopentene	14.56	82	693-89-0	0.21
12	1-Chloro-2-butene	16.07	90	591-97-9	0.30
13	1-Heptene	16.81	98	592-76-7	1.88
14	Cyclohexene	16.92	82	110-83-8	0.17
15	Benzene	17.75	78	71-43-2	1.06
16	5-Chloro-1-pentene	22.86	104	928-50-7	0.36
17	1-Octene	23.08	112	111-66-0	0.69
18	1,7-Octadiene	23.17	110	3710-30-3	0.31
19	Toluene	24.30	92	108-88-3	0.60
20	1-Nonene	28.21	126	124-11-8	0.49
21	1,8-Nonadiene	28.24	124	4900-30-5	0.10
22	1-Chloro-2-hexene	28.68	118	35911-16-1	0.36
23	1-Decene	32.50	140	872-05-9	10.78
24	3-Decene (Z) (or 5 decene?)	32.62	140	19398-86-8	0.15
25	3-Decene (E)	32.72	140	19150-21-1	0.20
26	2-Decene (Z)	32.88	140	20348-51-0	1.09
27	1,7-Dichloroheptane	33.15	168	821-76-1	0.17
28	2-Decene (E)	33.36	140	20063-97-2	0.78
29	1-Chlorooctane	36.82	148	111-85-3	0.40
30	8-Chloro-1-octene	36.97	146	N/A	0.25
31	1-Chlorodecane	43.63	176	1002-69-3	58.57

HCl is not seen in the chromatogram.

e = equatorial, a = axial) ( $\gamma$ -C<sub>6</sub>H<sub>6</sub>Cl<sub>6</sub>, lindane) is given in Figure 8.1.5. The experiment was performed on 0.25 mg compound using Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280^\circ\text{C}$ . The pyrolysate was analyzed by GC/MS under conditions given in Table 4.6.1. The compound identifications in the pyrogram and their relative molar content in 100 moles of pyrolysate are given in Table 8.1.2. The calculation of the mole percent was obtained based solely on peak areas.

As shown in Table 8.1.2, the main peaks in lindane pyrolysis belong to chlorinated benzenes. Lindane itself is present in the pyrolysate. Some of the parent compound was not pyrolyzed, probably because it evaporated before reaching a sufficiently high temperature to pyrolyze and was swept by the carrier gas passing through the pyrolyzer. The formation of chlorinated benzenes during the pyrolysis of lindane (and of other chlorinated pesticides) plays an important role in the formation of DLC compounds.

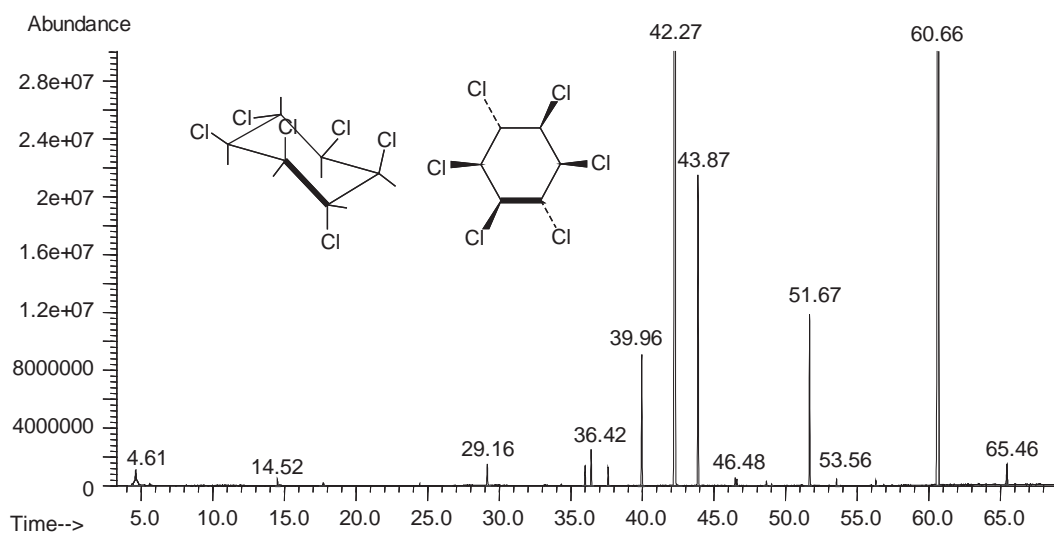


FIGURE 8.1.5. Pyrogram of  $\gamma$ -1,2,3,4,5,6-hexachlorocyclohexane (lindane,  $\gamma$ -C<sub>6</sub>H<sub>6</sub>Cl<sub>6</sub>) at 900°C. Peak assignment is given in Table 8.1.2.

TABLE 8.1.2. Identification of the main peaks in the chromatogram shown in Figure 8.1.5 for the pyrolysis of  $\gamma$ -1,2,3,4,5,6-hexachlorocyclohexane (lindane)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
	Air	4.61			
	Hydrocarbon impurity?	14.52			
1	Benzene	17.72	78	71-43-2	0.20
2	Chlorobenzene	29.16	112	108-90-7	0.98
3	1,3-Dichlorobenzene	35.99	146	541-73-1	0.61
4	1,4-Dichlorobenzene	36.42	146	106-46-7	1.14
5	1,2-Dichlorobenzene	37.61	146	95-50-1	0.58
6	1,2,4-Trichlorobenzene	39.96	180	120-82-1	3.44
7	1,3,5-Trichlorobenzene	42.27	180	108-70-3	40.72
8	1,2,3-Trichlorobenzene	43.87	180	87-61-6	8.83
9	1,2,4,5-Tetrachlorobenzene	46.48	214	95-94-3	0.18
10	1,2,3,5-Tetrachlorobenzene	46.59	214	634-90-2	0.16
11	1,2,3,4-Tetrachlorobenzene	48.66	214	634-66-2	0.10
12	3,4,5-Trichlorocyclohex-1-ene	49.02	184	N/A	0.03
13	1,3,4,5,6-Pentachlorocyclohex-1-ene	51.68	252	28903-24-4	3.22
14	3,4,5,6-Tetrachlorocyclohex-1-ene	53.56	218	1782-00-9	0.13
15	Pentachlorocyclohexene	56.31	252	319-94-8	0.06
16	$\gamma$ -Hexachlorocyclohexane (lindane)	60.66	288	58-89-9	39.23
17	$\delta$ -Hexachlorocyclohexane	65.46	288	319-86-8	0.39

HCl is not seen in the chromatogram.

Some aliphatic chlorinated hydrocarbons have aromatic rings or unsaturated moieties substituted on the same aliphatic structure that has the attached chlorines. These types of structures have a higher propensity to generate PCBs and PAHs by pyrolysis as compared to compounds not having such substitutions. A detailed discussion on pyrolysis of benzyl bromide used as an example of an aliphatic halogenated compound containing an aromatic ring is given in Section 8.2.

## 8.2. ALIPHATIC HYDROCARBONS SUBSTITUTED WITH OTHER HALOGENS

### General aspects

A variety of aliphatic hydrocarbons substituted with fluorine, bromine, iodine, or with combination of halogens (including chlorine) have practical applications. These compounds include intermediates in organic synthesis, monomers for various plastics, flame retardants, fire extinguishing agents, aerosol spray propellants, foam blowing agents, cleaning solvents, and refrigerant agents. Some of these uses were stopped because it was determined that certain halocarbon compounds are powerful greenhouse gases and have a depleting effect on the upper atmosphere ozone layer. Pyrolysis of aliphatic halocarbons may take place inadvertently during waste incineration or intentionally with the purpose of synthesis of other halogenated compounds. The mechanisms of pyrolysis of aliphatic hydrocarbons substituted with halogens other than chlorine show many similarities with that of chlorinated ones. However, the difference in the nature of the halogen may create some differences in the pyrolysis results because of the relatively large differences in the bond strength C–Halogen (or C–X). As shown in Table 3.1.1, the order of the bond energies is C–F (116 kcal/mol) > C–Cl (81 kcal/mol) > C–Br (68 kcal/mol) > C–I (51 kcal/mol). Both radicalic and concerted mechanisms are influenced by these energies. As shown in Section 2.2, the elimination of HX in a concerted mechanism ( $E_i$ ) leads to a transition state that may have a carbocation character, the elimination being not perfectly symmetrical. The difference in the halogen leads to different reaction rates of the elimination, which are typically in the order  $I > Br > Cl > F$ . The bond-energy differences also influence the reaction path during pyrolysis such that the concerted mechanism with the formation of a hydrohalogenated acid is favored in one case (if hydrogens are available), and the cleavage of a C–X bond is favored in another case. The differences in the heat of formation of HX (see Table 3.1.3) also may affect the preferred path of reaction.

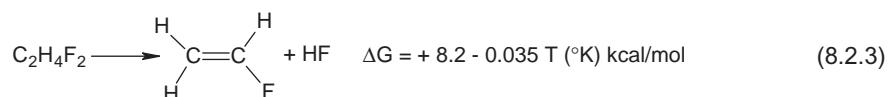
### Fluorinated compounds

Pyrolysis of fluoromethanes has been investigated with different goals, one of these being the understanding of the reactions that take place during flame suppression when these compounds are used. The pyrolysis process of fluoromethanes starts at temperatures around 900 °C, and because the C–F bond in fluorinated methanes is stronger with about 20 kcal/mol than the C–H bond, the reaction takes place with the elimination of a hydrogen atom (when present). For  $CH_3F$ , for example, the  $H^\bullet$  atoms will continue a propagation reaction, abstracting H atoms from  $CH_3F$  to generate  $H_2$  and new  $CH_2F^\bullet$  radicals as shown in the following reactions:



This reaction is different from that occurring for the other halogens, when the  $H^\bullet$  atoms would abstract the halogen. The abstraction of H atoms from fluoromethanes by  $H^\bullet$  also occurs in the case of  $CH_2F_2$  and  $CHF_3$  pyrolysis. The energy barrier for H abstraction has been calculated to be 11.8 kcal/mol for  $CH_3F$ , 9.7 kcal/mol for  $CH_2F_2$ , and 12.8 kcal/mol for  $CHF_3$ , while the abstraction of an atom of fluorine (to form HF) was calculated to be 31.4 kcal/mol for  $CH_3F$ , 34.1 kcal/mol for  $CH_2F_2$ , and 40.3 kcal/mol for  $CHF_3$  [33]. The  $CH_2F^\bullet$  radicals in a termination reaction will form  $C_2H_4F_2$ , which may continue with  $H_2$  elimination to form some  $C_2F_2$  and with reverse cleavage of the C–C bond to generate back  $CH_2F^\bullet$ . The elimination of HF from  $C_2H_4F_2$  with the formation of  $C_2H_3F$  starts to be an exothermic

reaction when the temperature increases above 0 °C and HF generation is favored by higher temperatures:



The exothermicity of HF elimination makes this reaction an important path in the pyrolysis of fluorinated ethanes and of other partly fluorinated compounds. The HF elimination takes place as long as hydrogen atoms are still available in the molecule. Radical mechanisms continue to be responsible for reactions at higher temperatures. For 1,2-difluoroethane, the formation of  $\text{C}_2\text{H}_3\text{F}_2^\bullet$  radicals by  $\text{H}^\bullet$  elimination leads to the production (low levels) of heavier fluorinated compounds in the pyrolysate.

Perfluorinated compounds undergo pyrolysis by free radicals formation and typically at temperatures higher than that for the equivalent hydrocarbon. The first bonds to be split are the C–C bonds, with the formation of smaller free radicals. However, the free radicals formed either by the cleavage of C–C bonds or of C–F bonds can interact and generate by propagation reactions compounds with higher molecular weight. For example, at temperatures around 655 °C,  $\text{C}_2\text{F}_4$  decomposes but at the same time generates  $\text{C}_3\text{F}_6$  with relatively good yield (42%). At higher temperatures  $\text{C}_4\text{F}_8$  is the major pyrolysis product [34].

Pyrolysis of a fluorinated compound containing one F atom substituted to a long-chain aliphatic hydrocarbon takes place very similarly to that of a chlorinated homolog (see Figure 8.1.4 and Table 8.1.1). As an example, the pyrogram of 1-fluorodecane is given in Figure 8.2.1. The experiment was performed in conditions similar to that of 1-chlorodecane. Pyrolysis was performed on 0.25 mg compound using Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ ,  $\text{THT} = 10\text{ s}$ , and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ . The analysis of pyrolysate was done under conditions given in Table 4.6.1. The compound identifications in the pyrogram and their relative molar content in 100 moles of pyrolysate are given in Table 8.2.1. The calculation of the mole percent was obtained based solely on peak areas.

The list of compounds resulting from the pyrolysis of 1-fluorodecane is very similar to that of 1-chlorodecane, with 1-decene the main pyrolysis product. Only the rate of HF elimination is somewhat lower than that of HCl elimination (as seen from the proportion of initial compound remaining in the pyrolysates). The decomposition of the two compounds is likely to follow the same mechanism.

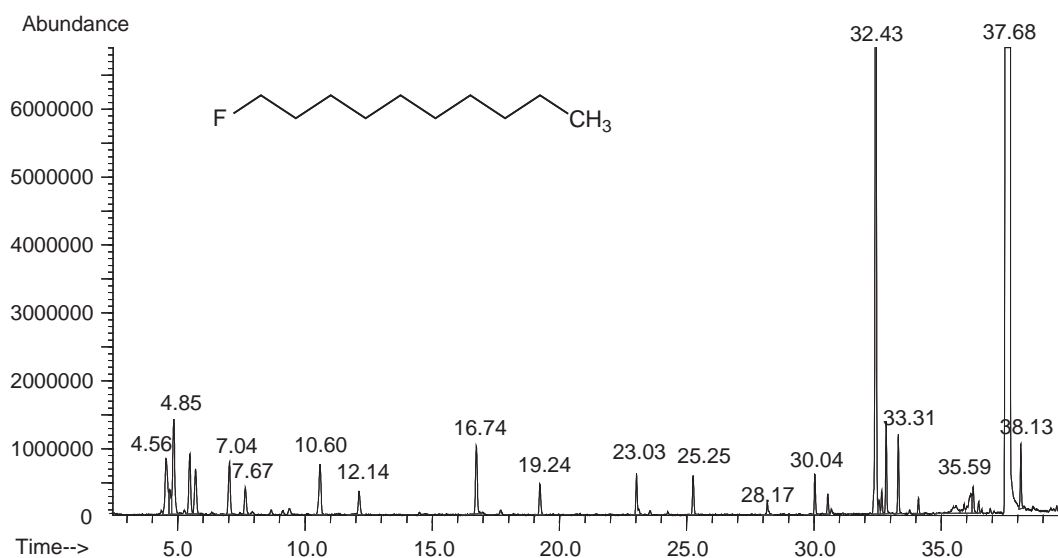


FIGURE 8.2.1. Pyrogram of 1-fluorodecane ( $\text{C}_{10}\text{H}_{21}\text{F}$ ) at  $900^\circ\text{C}$ . Peak assignment is given in Table 8.2.1.



TABLE 8.2.1. Identification of the main peaks in the chromatogram shown in Figure 8.2.1 for the pyrolysis of 1-fluorodecane ( $C_{10}H_{21}F$ )

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Hexafluoropropene	4.56	150	116-15-4	0.76
2	Fluoroethene	4.70	46	75-02-5	0.82
3	Propene	4.85	42	115-07-1	3.69
4	1-Butene	5.49	56	106-98-9	1.57
5	1,3-Butadiene	5.72	54	106-99-0	0.63
6	1-Fluoro-2-propene	5.73	60	818-92-8	0.57
7	1-Pentene	7.04	70	109-67-1	1.16
8	1-Fluoro-2-butene	7.67	74	N/A	0.52
9	1-Hexene	10.60	84	592-41-6	0.99
10	5-Fluoro-2-pentene	12.14	88	N/A	0.43
11	1-Heptene	16.74	98	592-76-7	0.92
12	Benzene	17.55	78	71-43-2	0.10
13	Mixture: fluorocyclohexan + fluorohexene	19.24	102	N/A	0.38
14	1-Octene	23.03	112	111-66-0	0.43
15	Fluoroheptene	25.25	116	N/A	0.34
16	1-Nonene	28.17	126	124-11-8	0.12
17	Fluorooctene	30.04	130	N/A	0.29
18	1-Decene	32.43	140	872-05-9	6.33
19	3-Decene (Z) (or 5 decene?)	32.56	140	19398-86-8	0.12
20	3-Decene (E)	32.66	140	19150-21-1	0.15
21	2-Decene (Z)	32.84	140	20348-51-0	0.58
22	2-Decene (E)	33.31	140	20063-97-2	0.51
23	Fluorononene	34.11	144	N/A	0.10
24	Hydrocarbon	36.59	140	N/A	0.38
25	1-Fluorodecane	37.68	160	334-56-5	77.76
26	Fluoroundecene?	38.13	172	N/A	0.33

HF is not seen in the chromatogram.

Applications of pyrolysis for various aliphatic hydrocarbons substituted with both fluorine and chlorine were reported in the literature [34,35]. The subject of these studies is typically related to the production of monomers such as tetrafluoroethylene and hexafluoropropene. When the fluorochloroalkane contains one or more hydrogen atoms, pyrolysis is dominated by dehydrochlorination. Depending on the relative position of the hydrogen and chlorine atoms, the process may be intramolecular or intermolecular. For example, chlorodifluoromethane ( $CHClF_2$ ) undergoes pyrolysis (with better yields on a  $AlF_3/CaF_2$  catalyst), the main result being  $C_2F_4$  in a reaction as follows:



The reaction starts with the formation of free radicals  $CHF_2^\cdot$  and  $CClF_2^\cdot$ . One potential path for the formation of  $C_2F_4$  is the termination reaction with the formation of  $CHCl_2-CClF_2$  (detected in traces in the pyrolysate) followed by HCl elimination. Alternative paths involve the formation of  $C_2H_2F_4$  and  $H_2$  elimination or formation of  $C_2Cl_2F_4$  and  $Cl_2$  elimination with the subsequent reaction of  $H_2$  and  $Cl_2$  to form HCl. Formation of  $CF_2^{\cdot\cdot}$  biradicals ( $\Delta H_f^\circ = -45 \text{ kcal/mol}$ ) followed by a termination reaction is another potential path. Direct pyrolysis of  $CHCl_2-CClF_2$  generates  $C_2F_4$  as well as  $C_4F_8$  and octafluorocyclobutane. Low levels of compounds with the general formula  $HCF_2-(CF_2)_n-CF_2Cl$  ( $n = 1, 2, \dots$ ) were also detected in the pyrolysate [36].

Pyrolysis of chlorofluoroalkanes with two or more carbon atoms and no hydrogen present in the molecule may proceed with the cleavage of the C–C bond. For example, pyrolysis of  $\text{CF}_2\text{Cl}-\text{CF}_2\text{Cl}$  yields a mixture of compounds including  $\text{CF}_2\text{Cl}_2$  and  $\text{CF}_3\text{Cl}$ , as well as  $\text{C}_2\text{F}_4$  and other unsaturated compounds.

The mechanism of dehydrochlorination of chloro-fluoro hydrocarbons was studied for 1-chloro-1-fluoroethane and 1-chloro-1,1-difluoroethane in the temperature range 500–600 °C [37]. The mechanism of decomposition was found to be unimolecular for both compounds, and kinetic data for these reactions are reported in the literature [37]. Pyrolysis of other more complex halogenated compounds was also studied, usually with the purpose of obtaining unsaturated fluorinated hydrocarbons that can be used as monomers in polymer industry. The study of 1,1,1-trifluoro-2-bromo-2-chloroethane pyrolysis showed that the process occurs with formation of 1,1,1-trifluoro-2-chloroethyl radical and of trifluoromethylcarbene with isomerization to trifluoroethylene [38].

### Brominated compounds

Brominated compounds decompose by pyrolysis in a way very similar to the chlorinated ones. Brominated methanes decomposition is initiated by a unimolecular process involving the cleavage of a C–Br bond [39]. Ethyl bromide decomposes with the formation of HBr and ethene, the only difference from ethyl chloride pyrolysis being a slightly lower decomposition temperature. The same effect as for chlorine derivatives of back-reaction of HX with the generated alkene is seen in the case of bromine derivatives. This effect seems to be even more frequent for brominated hydrocarbons. Some transpositions of bromine from primary to secondary or to tertiary carbons are seen even at lower temperatures than those involved during pyrolysis.

Pyrolysis of a compound containing one Br atom substituted to a long-chain aliphatic hydrocarbon takes place very similarly to that of a chlorinated or fluorinated homolog (see Figure 8.1.4 and Table 8.1.1). As an example, the pyrogram of 1-bromodecane is given in Figure 8.2.2. The experiment was performed in conditions similar to those for 1-chlorodecane. Pyrolysis was performed on 0.35 mg compound using Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ . The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications in the pyrogram and their relative molar content in 100 moles of pyrolysate are given in Table 8.2.2. The calculation of the mole percent was obtained based solely on peak areas.

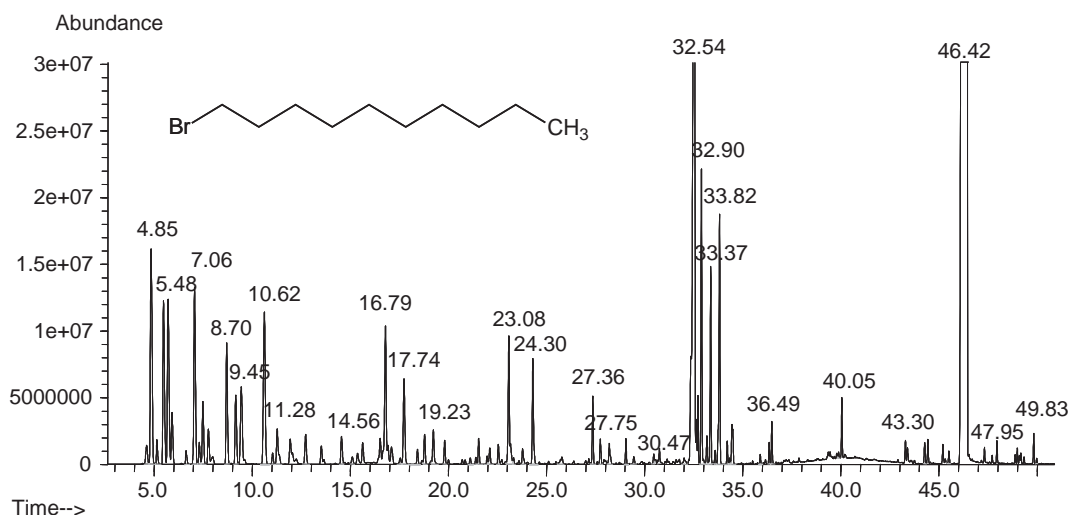


FIGURE 8.2.2. Pyrogram of 1-bromodecane ( $\text{C}_{10}\text{H}_{21}\text{Br}$ ) at  $900^\circ\text{C}$ . Peak assignment is given in Table 8.2.2.

TABLE 8.2.2. Identification of the main peaks in the chromatogram shown in Figure 8.2.2 for the pyrolysis of 1-bromodecane ( $C_{10}H_{21}Br$ )

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Propene	4.85	42	115-07-1	9.03
2	Cyclopropane	5.15	42	75-19-4	0.75
3	1-Butene	5.48	56	106-98-9	4.79
4	1,3-Butadiene	5.72	54	106-99-0	5.22
5	2-Butene	5.92	56	107-01-7	1.50
6	Bromomethane	6.64	94	74-83-9	0.21
7	1-Pentene	7.06	70	109-67-1	4.23
8	Vinylbromide	7.30	106	593-60-2	0.34
9	1,2-Dimethylcyclopropane	7.49	70	930-18-7	1.37
10	2-Pentene	7.77	70	646-04-8	0.81
11	2-Methyl-1,3-butadiene	7.99	68	78-79-5	0.31
12	1,3-Pentadiene	8.70	68	504-60-9	2.75
13	1,4-Pentadiene	9.16	68	591-93-5	1.56
14	Cyclopentene	9.44	68	142-29-0	1.00
15	Cyclopentadiene	9.45	66	542-92-7	1.07
16	1-Hexene	10.62	84	592-41-6	3.51
17	3-Hexene (Z)	11.04	84	7642-09-3	0.21
18	2-Hexene	11.28	84	4050-45-7	0.85
19	3-Hexene (E)	11.94	84	13269-52-8	0.55
20	3-Methylcyclopentene	12.05	82	1120-62-3	0.27
21	Methylcyclopentane	12.72	84	96-37-7	0.64
22	1,3-Hexadiene	13.52	82	592-48-3	0.27
23	1-Methylcyclopentene	14.56	82	693-89-0	0.57
24	Cyclohexane	15.10	84	110-82-7	0.16
25	2-Bromopropane	15.37	122	75-26-3	0.18
26	2,4-Hexadiene (E,Z)	15.63	82	5194-50-3	0.40
27	2,4-Hexadiene (Z,Z)	16.53	82	6108-61-8	0.57
28	1-Heptene	16.79	98	592-76-7	2.40
29	Cyclohexene	16.92	82	110-83-8	0.33
30	3-Heptene (E)	17.10	98	592-78-9	0.37
31	Benzene	17.74	78	71-43-2	1.88
32	2-Heptene (E)	18.42	98	14686-13-6	0.22
33	3,5-Dimethylcyclopentene	18.65	96	7459-71-4	0.00
34	Butylcyclopropane	18.79	98	930-57-4	0.44
35	Methylcyclohexane	19.23	98	108-87-2	0.60
36	1,4-Heptadiene	20.01	96	5675-22-9	0.07
37	1-Methylcyclohexene	20.70	96	591-49-1	0.05
38	4-Methylcyclohexene	20.86	96	591-47-9	0.00
39	4,4-Dimethylcyclopentene	21.11	96	19037-72-0	0.10
40	1-Ethylcyclopentene	21.40	96	2146-38-5	0.10
41	4-Bromo-1-butene	21.54	134	5162-44-7	0.25
42	2-Methyl-1,4-hexadiene	21.97	96	1119-14-8	0.12
43	1-Bromobutane	22.11	136	109-65-9	0.19

TABLE 8.2.2. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
44	3-Methylcyclohexene	22.54	96	591-48-0	0.27
45	1-Octene	23.08	112	111-66-0	1.77
46	1,7-Octadiene	23.17	110	3710-30-3	0.17
47	3-Octene	23.32	112	14850-22-7	0.09
48	2-Octene	23.78	112	2097322	0.24
49	Toluene	24.30	92	108-88-3	1.49
50	Cyclooctene?	25.79	110	931-88-4	0.21
51	1,2-Dimethylcyclooctene	27.00	110	1674-10-8	0.00
52	2,4-Octadiene	27.16	110	13646-08-8	0.09
53	5-Bromo-1-pentene	27.36	148	1119-51-3	0.53
54	1-Bromopentane	27.75	150	110-53-2	0.22
55	1-Nonene	28.21	126	124-11-8	0.29
56	Ethylbenzene	29.05	106	100-41-4	0.27
57	1,3-Dimethylbenzene ( <i>m</i> -xylene)	29.45	106	108-38-3	0.13
58	<i>cis</i> -3-decene	30.47	140	19398-86-8	0.12
59	1,4-Dimethylbenzene ( <i>p</i> -xylene)	30.76	106	106-42-3	0.22
60	Styrene	31.16	104	100-42-5	0.07
61	2-Decene (Z)	32.02	140	20348-51-0	0.12
62	1-Decene	32.54	140	872-05-9	10.53
63	3-Decene (Z) (or 5 decene?)	32.64	140	19398-86-8	0.32
64	3-Decene (E)	32.72	140	19150-21-1	0.44
65	2-Decene (Z)	32.90	140	20348-51-0	2.16
66	1-Methyl-2-propylcyclohexane?	33.18	140	4291-79-6	0.25
67	2-Decene (E)	33.37	140	20063-97-2	1.35
68	1,2-Dimethylcyclooctane?	33.60	140	13151-94-5	0.11
69	Cyclodecane	33.82	140	293-96-9	1.99
70	1-Methyl-3-propylcyclohexane	34.21	140	4291-80-9	0.18
71	1,2-Diethylcyclohexane	34.33	140	824-43-1	0.05
72	Pentylcyclopentane	34.46	140	3741-00-2	0.28
73	Butylcyclohexane	34.53	140	1678-93-9	0.22
74	1-Methyl-4-(1-methylethyl)cyclohexane?	35.90	140	1678-82-6	0.08
75	1-Bromoheptane	36.35	178	629-04-9	0.12
76	10-Bromo-1-decene	36.49	218	62871-09-4	0.21
77	1-Bromooctane	39.89	192	111-83-1	0.04
78	8-Bromo-1-octene	40.05	190	2695-48-9	0.29
79	1-Bromononane + impurity	43.30	206	N/A	0.10
80	3-Bromodecane	44.28	220	30571-71-2	0.10
81	?-Bromodecane	44.44	204	N/A	0.12
82	1-Bromodecane	46.42	220	112-29-8	24.50

HBr is not shown in the pyrogram.

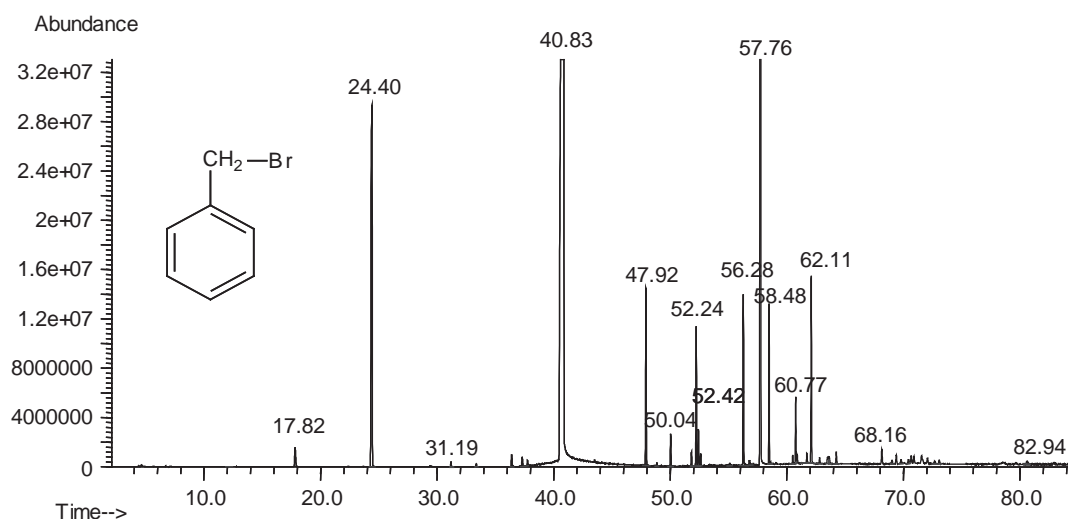
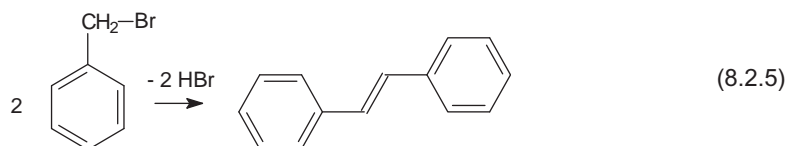


FIGURE 8.2.3. Pyrogram of benzyl bromide at 900 °C. Peak assignment is given in Table 8.2.3.

The list of compounds resulting from the pyrolysis of 1-bromodecane is very similar to that of 1-chlorodecane, although the pyrolysate seems to be more complex and the list from Table 8.2.2 contains more compounds. The rate of HBr elimination is higher than the elimination of HF from 1-fluorodecane and higher than that of HCl from 1-chlorodecane (as seen from the proportion of initial compound 1-bromodecane remaining in the pyrolysates). The apparent higher complexity of the pyrolysate from 1-bromodecane was very likely caused by the higher rate of decomposition, which generated higher levels of the pyrolysate constituents relative to the parent compound. The same compounds (with different halogen substitutions) but at lower levels were probably present in the pyrolysate of the other 1-halogenated decanes, but some components were not detected in the pyrolysates because of the set threshold of detection in the GC/MS analysis.

A peculiar case of aliphatic halogenated compounds appears when aromatic or unsaturated moieties are attached to the aliphatic chain that also contains halogen substitutions. The presence of aromatic moieties brings these compounds closer to the structures of PCBs and PAHs, and the presence of halogens increases the propensity for intramolecular eliminations. For these reasons, the generation of PCBs and PAHs is typically increased when in addition to the halogens an aromatic structure is present on the aliphatic chain. One example is the pyrolysis of benzyl bromide. The pyrogram for this compound is given in Figure 8.2.3. The experiment was performed on 0.50 mg compound using Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900\text{ }^{\circ}\text{C}$ ,  $\beta = 10\text{ }^{\circ}\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280\text{ }^{\circ}\text{C}$ . The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications in the pyrogram and their relative molar content in 100 moles of pyrolysate are given in Table 8.2.3. The calculation of the mole percent was obtained based solely on peak areas. The purity of the parent molecule was verified by GC/MS, and the only detected impurities were low levels of benzyl chloride and a trace of benzaldehyde.

As shown in Table 8.2.3, the main decomposition products of benzyl bromide are toluene and stilbene. Formation of stilbene is the result of HBr elimination between two benzyl bromide molecules:



The formation of phenanthrene from stilbene takes place easily by further  $\text{H}_2$  elimination. Other PAHs can be formed by similar reactions from precursors such as triphenylethylene and diphenylindanes. Specific PAHs such as 9-benzylanthracene and 4,5-dihydro-benzo[a]pyrene are

TABLE 8.2.3. Identification of the main peaks in the chromatogram shown in Figure 8.2.3 for the pyrolysis of benzyl bromide

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Benzene	17.82	78	71-43-2	1.04
2	Toluene	24.40	92	108-88-3	21.68
3	Styrene	31.19	104	100-42-5	0.13
4	Bromobenzene	33.36	156	108-86-1	0.06
5	Benzyl bromide	40.83	170	100-39-0	50.16
6	Biphenyl	48.85	154	92-52-4	0.05
7	Diphenylmethane	50.04	168	101-81-5	0.45
8	1,1-Diphenylethylene	51.83	180	530-48-3	0.18
9	1-Methyl-4-(phenylmethyl)benzene	52.24	182	620-83-7	1.86
10	Bibenzyl	52.42	182	103-29-7	0.50
11	1-Methyl-3-(phenylmethyl)benzene	52.62	182	620-47-3	0.15
12	Fluorene	55.12	166	86-73-7	0.05
13	Diphenylethyne	56.28	178	501-65-5	2.28
14	(E)-stilbene	57.76	180	103-30-0	15.58
15	1-Bromo-3-(2-phenylethenyl)benzene	58.48	258	14064-45-0	1.44
16	1,1'-(1-Bromo-1,2-ethenediyl)bisbenzene	58.62	258	40389-50-2	0.02
17	9-Methylene-9H-fluorene	60.52	178	4425-82-5	0.15
18	Phenanthrene	60.77	178	85-01-8	0.99
19	1-Bromo-4-(2-phenylethenyl)benzene	62.11	258	13041-70-8	1.97
20	1,1'-(1,2-Dibromo-1,2-ethenediyl)bisbenzene	63.51	336	32047-17-9	0.20
21	?-Bromo-?--(2-phenylethenyl)benzene	64.25	258	N/A	0.14
22	Triphenylethylene	68.16	256	58-72-0	0.21
23	Methyltriphenylethylene	69.40	270	N/A	0.14
24	1,4-Bis(phenylmethyl)benzene	69.81	258	793-23-7	0.07
25	2,3-Dihydro-1,2-diphenyl-1H-indene	71.57	270	34987-62-7	0.19
26	1,3-Bis(phenylmethyl)benzene	72.70	258	N/A	0.05
27	1,3-Diphenylindane	73.09	270	N/A	0.06
28	9-Benzylanthracene	78.59	268	1498-71-1	0.09
29	4,5-Dihydro-benzo[a]pyrene	82.94	254	57652-66-1	0.09

HBr is not shown in the pyrogram.

detected in the pyrolysate. The example of benzyl bromide pyrolysis shows, once more, that the structure of a molecule and the pyrolysis results are highly interrelated, the whole structure of the parent molecule playing an important role in the outcome of the process.

### ***Iodinated compounds***

Iodine derivatives of aliphatic hydrocarbons are only to a certain extent similar to the other halogenated compounds. One typical characteristic is their lower thermal stability. Ethyl iodide, for example, starts

decomposing at temperatures as low as 190 °C. In addition, because HI easily decomposes into hydrogen and iodine, this compound is not typically found in pyrolysates. Also, elimination of HI is not always favored before a C–I cleavage. At 230 °C the decomposition of ethyl iodide, for example, occurs as follows:



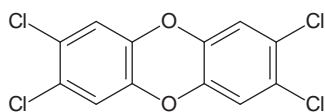
At higher temperatures,  $\text{C}_2\text{H}_4\text{I}_2$  also decomposes to form  $\text{C}_2\text{H}_4$  and iodine. The reaction products at temperatures around 300 °C and extended heating times for ethyl iodide are  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ , and  $\text{I}_2$ . Formation of  $\text{I}_2$  is typical also for the decomposition of  $\text{C}_2\text{I}_4$ , which by heating decomposes initially into  $\text{C}_2\text{I}_2$  and further into carbon and iodine, such that the end result of pyrolysis is the decomposition into elements.

Besides the common compounds of monovalent iodine, organic compounds containing iodine in a higher valence state (three) are known. The hydrocarbon moiety can be aliphatic or aromatic. Phenyl iodide chloride ( $\text{C}_6\text{H}_5\text{ICl}_2$ ) is relatively stable, decomposing around 120 °C with the formation of HCl and *p*-chloriodobenzene, while the alkyl iodide chlorides ( $\text{R-ICl}_2$ ) are not very stable even at room temperature.

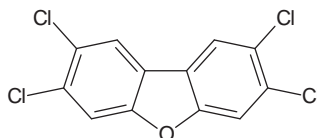
### 8.3. HALOGENATED AROMATIC HYDROCARBONS

#### *Preliminary information*

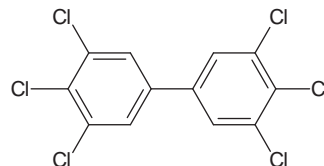
The replacement in an aromatic hydrocarbon of one or more hydrogen atoms with chlorine atoms leads to the class of aromatic chlorinated hydrocarbons. Similar to the case of chlorinated aliphatic hydrocarbons, the number of possibilities of hydrogen replacements is high. For example, there are 209 possible congeners of chlorinated biphenyls. Each congener has an IUPAC number assigned [40]. A large number of organic compounds that are used in practice contain in their molecule a chlorinated aromatic moiety, with or without the addition of other functionalities. Such compounds are used as pesticides, herbicides, disinfectants, pharmaceuticals, etc. A particular group of chlorinated aromatic hydrocarbons are the PCBs. PCBs were used as stabilizing additives in plastics, coolants and insulating fluids for electricity transformers and capacitors, cutting oils, hydraulic fluids, adhesives, etc. Most PCBs are toxic compounds and are classified as persistent organic pollutants. Besides their intentional synthesis, which has been banned, unintentional formation of PCBs occurs in various pyrolytic processes. Pyrolysis of chlorinated aromatic hydrocarbons, in general, is strongly related to the formation of chlorinated dibenzo-*p*-dioxins, chlorinated dibenzofurans, and PCBs (DLCs). Oxidative pyrolysis and the presence of a solid support during pyrolysis may increase the generation of DLCs. As indicated in Section 2.1, the resemblance between the initial molecule and the pyrolysis products is frequently obvious. Aromatic chlorinated compounds can generate DLCs more easily compared to the chlorinated aliphatic halocarbons. This can be seen from the similarity of chlorinated benzene to that of a dioxin, furan, or a PCB, with example structures shown below:



2,3,7,8-tetrachlorodibenzo-*p*-dioxin



2,3,7,8-tetrachlorodibenzofuran



3,3',4,4',5,5'-hexachlorobiphenyl

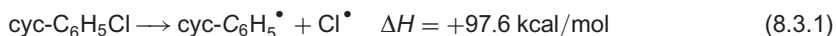
By pyrolysis in an inert atmosphere and in the absence of other components, chlorodibenzodioxins are generated only if oxygen functionalities are present in a halogenated molecule (e.g., from a chlorophenol or bromophenol) [5,6]. On a solid support that also has the potential to act as a catalyst and in

the presence of moisture, chlorobenzenes with no additional functionalities can generate chlorodibenzodioxins and chlorodibenzofurans [12].

### Chlorobenzenes

Various degrees of substitution with chlorine of the hydrogens from a benzene molecule lead to 12 possible compounds. These include monochlorobenzene (chlorobenzene), three dichlorobenzene isomers, three trichlorobenzene isomers, three tetrachlorobenzene isomers, pentachlorobenzene, and hexachlorobenzene. Pyrolysis of this group of compounds is the subject of various studies [41–50]. Detailed results on the pyrolysis of chlorobenzene in the range of 1000–1400 °C were reported for an experiment that was performed using a flow reactor with a 1 m long heated tube with an internal diameter of 15 mm and a constant flow through such that the residence time at 1000 °C was 1.6 s and at 1400 °C was 1.1 s. Chlorobenzene was diluted with N<sub>2</sub> such that its concentration was 0.59% (molar) at the reactor entrance [41]. As expected, the increase in temperature led to a faster decomposition. Hydrogen, HCl, benzene, acetylene, and methane were the main pyrolysis products, as shown in Figure 8.3.1.

Other compounds detected in the pyrolysate at low or trace levels included ethylene, cyclopentadiene, acetylbenzene, dichlorobenzene, biphenyl, *ortho*-chlorobiphenyl, *meta*-chlorobiphenyl, *para*-chlorobiphenyl, dichlorobiphenyls, naphthalene, chloronaphthalene, and acenaphthylene. Soot also was produced during pyrolysis. A separate study showed that carbon formation starts to be noticed around 850 °C and increases up to 50% of chlorobenzene at 1170 °C [49]. The main initiation reaction for chlorobenzene pyrolysis is very likely the formation of free phenyl radicals and atomic chlorine:



This reaction is further continued with the formation of HCl and a new set of radicals, as shown below:

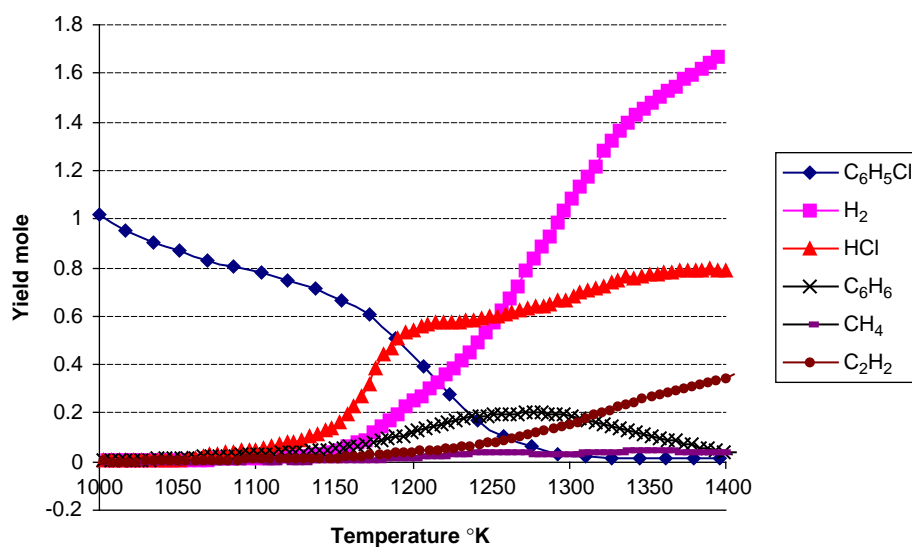
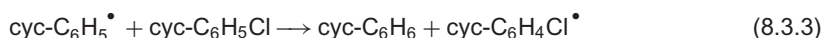


FIGURE 8.3.1. Variation in the molar composition (relative to the parent molecule) of chlorobenzene pyrolysate (0.59% molar in N<sub>2</sub>) in a flow reactor with 1.6–1.1 s residence time [41].



The kinetic law for HCl formation is expressed by the formula  $k = 10^{10.9} \exp(-29,000/T) \text{ s}^{-1}$ . The route of formation of  $\text{C}_6\text{H}_4\text{Cl}^\bullet$  (*ortho*, *meta*, or *para*) radicals by direct cleavage of a C–H bond is less favored since this reaction is more endothermic (120.8 kcal/mol) than reaction 8.3.1. However, there is a limited proportion of Cl atoms relative to H atoms in the molecule of chlorobenzene, and, as seen from Figure 8.3.1, hydrogen and benzene are among the main pyrolysis products of this compound. The formation of benzene can be explained by the reaction:

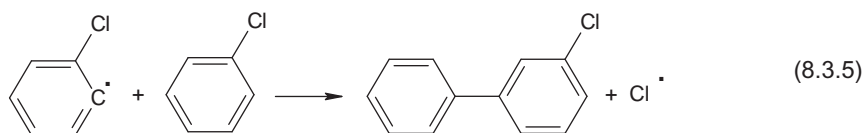


The formation of  $\text{H}_2$  indicates that as the temperature increases, the formation of  $\text{C}_6\text{H}_4\text{Cl}^\bullet$  free radicals and hydrogen atoms also takes place by the reaction:

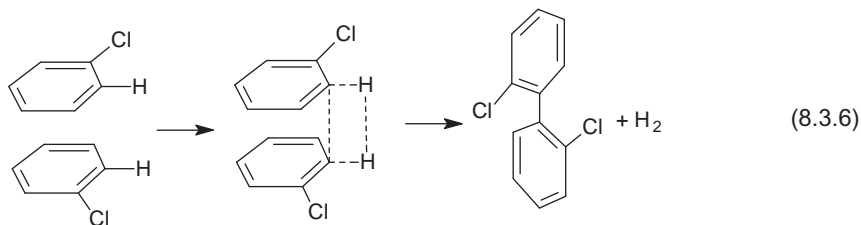


The  $\text{H}^\bullet$  atoms promote the formation of more free radicals and also of  $\text{H}_2$  when chlorine is no longer available for HCl formation. Molecular hydrogen also can be generated from benzene pyrolysis as a secondary reaction (see Section 7.7).

A termination reaction between  $\text{C}_6\text{H}_5^\bullet$  radicals is a source of biphenyls, termination between  $\text{C}_6\text{H}_4\text{Cl}^\bullet$  radicals is a source of dichlorobiphenyls (six isomers), and the termination reaction between  $\text{C}_6\text{H}_4\text{Cl}^\bullet$  and  $\text{C}_6\text{H}_5^\bullet$  is a source of chlorobiphenyls (three isomers) [42]. Propagation reactions can be of the type shown below:



These types of propagation reactions are also responsible for the formation of chlorinated biphenyls. The level of chlorobiphenyls is the highest around 900 °C, and at higher temperatures their level starts to decrease. The relative ratios of *ortho*, *meta*, and *para* forms for pyrolysis between 1000 °C and 1400 °C was reported to be 12/63/25 [41] and for pyrolysis at 500 °C was reported to be 21/52/27 [51]. The reaction between two chlorobenzene molecules with the formation of chlorobiphenyls or dichlorobiphenyls by a concerted mechanism is not impossible, considering that not all chlorine from the organic compound is present as HCl in the pyrolysate, as would be expected based on the heats of formation involved in the reactions. A concerted mechanism reaction for the formation of dichlorobiphenyl can be written as follows:



The potential occurrence of reactions of the type (8.3.6) can be justified by the lower activation energies involved in the process. A model calculation for the reaction of benzene with fluorobenzene to generate biphenyl and HF indicated an activation energy of the order of 30 kcal/mol. The variation of energy along the reaction path (coordinate) between benzene and fluorobenzene as calculated using the package MOPAC-7 [52] with AM1 parameterization is shown in Figure 8.3.2.

An interesting aspect of chlorobenzene pyrolysis is the formation of  $\text{CH}_4$  and  $\text{C}_2\text{H}_2$ , which are present among the main pyrolysis products. The formation of  $\text{C}_2\text{H}_2$  is explained easily by the decomposition of benzene initially formed by reaction 8.3.3 and further decomposed, as shown in

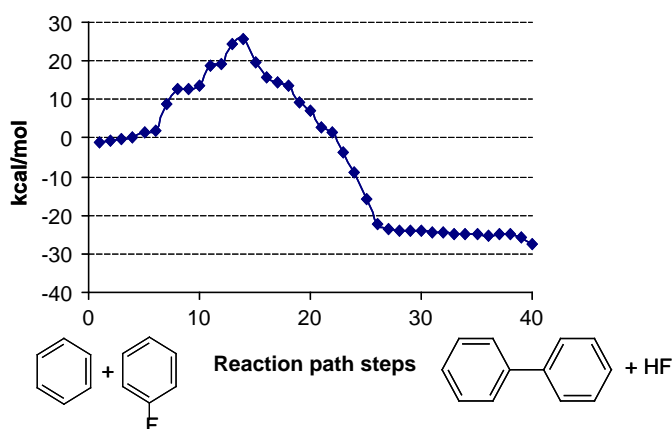
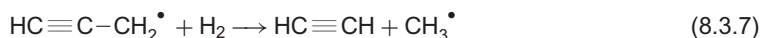


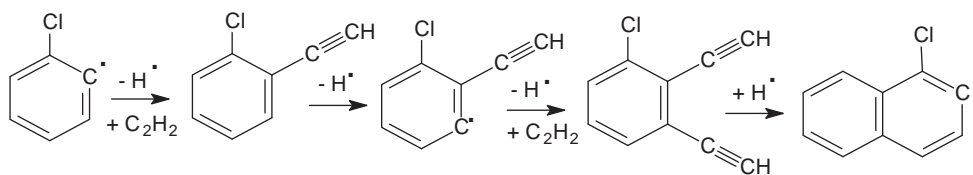
FIGURE 8.3.2. Variation of energy along the reaction path (coordinate) for benzene + fluorobenzene interaction.

reactions 7.7.5 and 7.7.6. Methane possibly results after the formation of propargyl radicals from the methyl radicals that are generated in reactions of the type:

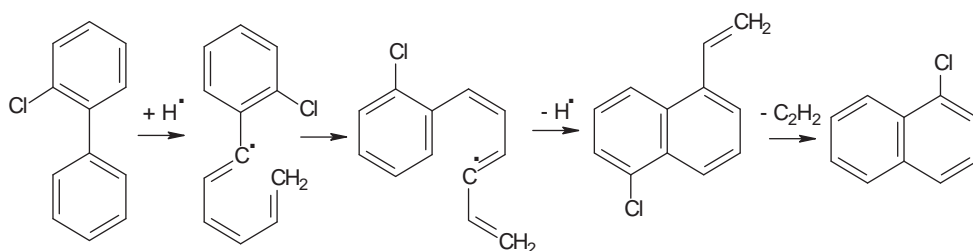


The presence of acetylene and benzene explains the formation by HACA-type reactions of naphthalene and acenaphthylene in chlorobenzene pyrolysate. An alternative route for acetylene formation starts with the formation of a cyclohexadienyl radical resulting from reactions similar to 7.7.4 (see Section 7.7).

The formation of chloronaphthalene can be explained by HACA-type reactions between acetylene and chlorobenzene:



Other reaction paths are possible, such as the one starting with chlorobiphenyl and involving the opening of one of the benzene rings upon reacting with a hydrogen atom, as shown below:

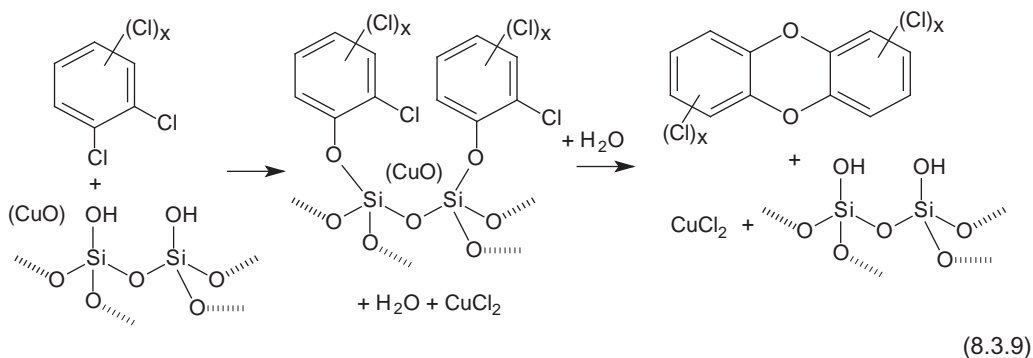


(8.3.8)

The formation of chloronaphthalene and of chlorobiphenyls is influenced equally by the variation in the pyrolysis temperature [41]. The formation of chlorovinyl naphthalene as an intermediate compound

may explain the formation of acenaphthylene among the pyrolysis products of chlorobenzene. Starting with *meta*-chlorobiphenyl in reaction 8.3.8, the resulting intermediate compound 1-chloro-8-vinylnaphthalene can generate acenaphthylene by HCl elimination. Naphthalene can be formed from 1-chloronaphthalene by reactions similar to those from which benzene is formed from chlorobenzene.

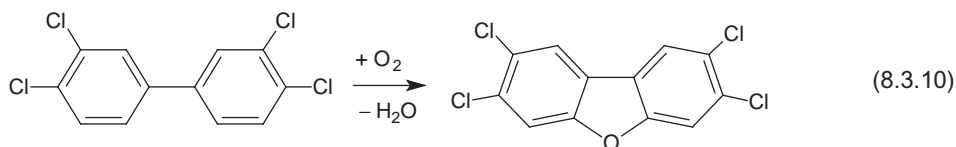
Other studies were focused on the yield of formation of PCBs by pyrolysis from various chlorobenzenes [53]. Formation of DLCs in the presence of catalysts also has been evaluated. The formation of chlorinated dibenzodioxins on a SiO<sub>2</sub> support and in the presence of a catalyst (such as CuO) can take place as shown below [12]:



Reactions similar to 8.3.9 explain why the generation of dioxin and other DLCs is higher than expected in industrial incinerators that handle considerable quantities of solids [54]. Chlorobenzenes can generate PCDFs by reactions similar to reaction 8.3.9 [55].

### Other halogenated aromatic hydrocarbons

Various studies are reported in the literature regarding other halogenated aromatic hydrocarbons. Pyrolysis in the absence of oxygen and/or catalysts occurs at relatively high temperatures for polychlorinated compounds with more aromatic rings. For example, chloronaphthalene starts to decompose with noticeable results above 950 °C. Some halogenated aromatic hydrocarbons were studied in connection with the molecular growth during pyrolysis and in relation to synthesis of specific organic compounds using pyrolytic techniques. An interesting reaction performed on 1,1-dichloroperfluorotetralin showed, for example, that thermal decomposition of this compound takes place with elimination of CHClF<sub>2</sub> [56]. Most of the studies performed on halogenated compounds with more than one aromatic cycle were related to the formation of DLCs from halogenated derivatives with lower TEF [57–59]. Mineral oils containing PCBs (marketed under the name Aroclor) can generate, under pyrolytic and oxidative conditions, PCDFs in a reaction as shown below:



Other studies dealt with the formation of DLCs from flame retardants, some of these compounds being brominated or chlorinated aromatic compounds including polybrominated diphenyl ethers, polybrominated biphenyls (PBBs), and certain brominated cyclohydrocarbons [60–62]. The use of catalyst and reductive pyrolysis for dehydrochlorination of PCBs has been proposed with the purpose of reducing their levels in oxidative pyrolytic processes [63].

Besides pyrolysis of pure aromatic halogenated hydrocarbons, the study of some industrially produced PCB has been reported in the literature [64,65]. One example is the study of pyrolysis of

Aroclor 1254. This material is a PCB mixture containing approximately 21%  $C_{12}H_6Cl_4$ , 48%  $C_{12}H_5Cl_5$ , 23%  $C_{12}H_4Cl_6$ , and 6%  $C_{12}H_3Cl_7$  with an average chlorine content of 54%. Pyrolysis of Aroclor 1254 performed in an airflow either in a flame or in a quartz tube at 500, 600, and 700 °C showed that a complex mixture of compounds is generated [64]. The pyrolysate contains non-oxygenated halogenated aromatic hydrocarbons, but because of the presence of oxygen, it also contains mono-, di-, tri-, tetra-, and pentachlorophenols; mono-, di-, tri-, and tetrachlororesorcinols; and mono-, di-, tri-, and tetrachlorohydroquinones.

### Halogenated aromatic heterocyclic compounds

Heterocyclic aromatic compounds contain in their molecules at least one heteroatom and one carbon (see Chapter 21). Hydrogens connected to carbon atoms are frequently part of the heterocyclic molecules. Substitution of these hydrogen atoms with halogens leads to halogenated aromatic heterocyclic compounds. The molecules from this class are typically as stable as halogenated compounds of homocyclic aromatic compounds. Thermal decomposition of heterocyclic compounds affecting the aromatic ring is discussed in Chapter 21. Some studies on halogenated aromatic heterocycles are reported in the literature [22]. Chlorinated (and brominated) dibenzo-*p*-dioxins and dibenzofurans are halogenated heterocycles particularly stable to degradation.

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## CHAPTER 9

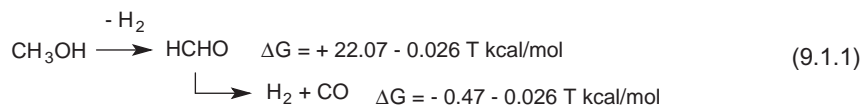
*Pyrolysis of Alcohols and Phenols***9.1. ALCOHOLS****General aspects**

The replacement in a hydrocarbon of one or more hydrogen atoms with OH groups forms alcohols, enols, or phenols, depending on the nature of the carbon to which the OH group is attached. The compounds having the OH group attached to a carbon with  $sp^3$  hybridization are alcohols, even if the aliphatic structure contains unsaturation at other carbons or is substituted with aryl groups (such as in benzyl alcohol  $C_6H_5-CH_2OH$ ). In phenols, the carbon to which the OH is attached is part of an aromatic ring (made of carbon atoms) sometimes indicated as Ar. In enols, the carbon connected to the OH has an  $sp^2$  hybridization (is involved in a double bond). Depending on the number of substitutions on the carbon to which the OH is attached, the alcohols are classified as primary (OH attached to a primary carbon atom), secondary, or tertiary.

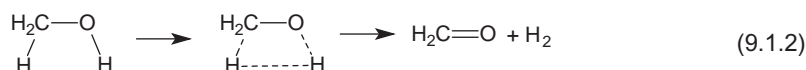
A large number of alcohols have practical applications. The best-known compound from this class is probably ethyl alcohol. Besides its use in alcoholic beverages, ethyl alcohol (ethanol) is used as a fuel, as a solvent, etc. Other alcohols such as methanol are used in various important industrial processes. A variety of alcohols are present (in free form) in nature. Among these are short-chain alcohols (resulting from fermentation processes of glucides), alcohols with long aliphatic carbon chain present in plant cuticles, cycloaliphatic alcohols such as menthol also present in plants, etc. Pyrolysis of alcohols is related to a variety of processes including industrial synthesis of specific compounds, pyrolysis during waste incineration or accidental fires, and use as fuels.

**Short-chain monohydroxy primary alcohols**

Methanol ( $CH_3OH$ ) or methyl alcohol is stable to heating up to about  $500^\circ C$ . Above this temperature it generates mainly formaldehyde, CO, and  $H_2$ . The main reactions taking place during pyrolysis are the following:



The reaction mechanism for the formation of formaldehyde (HCHO) does not appear to be radicalic since no ethane or ethylene is formed during pyrolysis. The reaction seems to take place by a concerted elimination as shown below:



A detailed study regarding pyrolysis and oxidation of methanol at several methanol/oxygen ratios ( $\Phi = 0.7, 1.0, 1.5$ ) as well as in the absence of oxygen ( $\Phi = \infty$ ) and at temperatures between  $300^\circ C$  and  $1000^\circ C$  has been reported in the literature [1]. In addition to the previously reported decomposition products of methanol ( $H_2$ , CO, HCHO), trioxane was found among the pyrolysis products (as a result of formaldehyde trimerization). The variation in the relative level of main pyrolysis products of methanol as a function of temperature in the absence of oxygen is given in Figure 9.1.1 (hydrogen not shown).

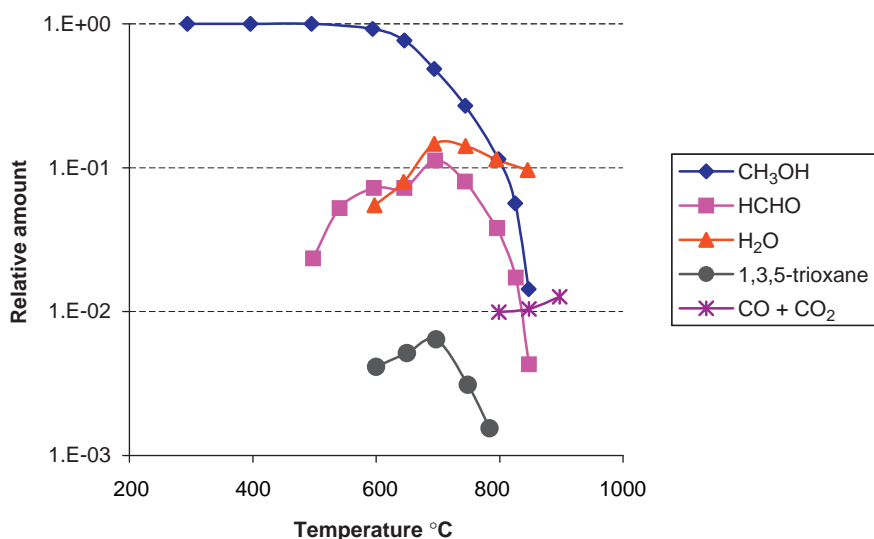


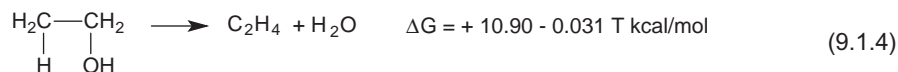
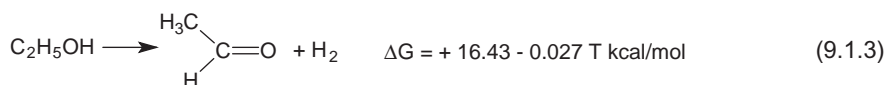
FIGURE 9.1.1. Relative distribution as a function of temperature of the main pyrolysis products for a sample of  $\text{CH}_3\text{OH}$  with initial concentration 1580 ppm (smooth interpolation of data) at 2 s residence time in a flow experiment ( $\Phi = \infty$ ). The variation in the level of hydrogen is not shown [1].

The experiment was carried out in a quartz cylindrical flow reactor with a residence time of 2 s. The initial concentration of methanol was 1580 ppm [1].

As pyrolysis temperature increases, some  $\text{CO}_2$  is seen in the pyrolysates together with traces of  $\text{CH}_4$ . These compounds can be the result of an oxidation–reduction reaction between two  $\text{HCHO}$  molecules or the result of other secondary processes. In the presence of oxygen ( $\Phi = 0.7$ ), some acetone also is detected in the oxidative pyrolysis products.

The formation of  $\text{HCHO}$  from methanol is performed on an industrial scale, but the procedure involves an oxidation in the presence of catalysts (Ag metal or Fe, Mo, and V oxides). Formaldehyde can be oxidized easily to formic acid in the presence of oxygen, and the process should be controlled to avoid this result in formaldehyde production. Other studies were related to the combustion of methanol, either pure or in mixture with other compounds such as single alkanes, gasoline and diesel fuels, etc., and are reported in the literature [2–6].

Pyrolysis of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) begins around 550 °C. Two reactions dominate thermal decomposition of ethanol, one being dehydrogenation and the other water elimination. The two reactions, which are also characteristic for other alcohols, are shown below:

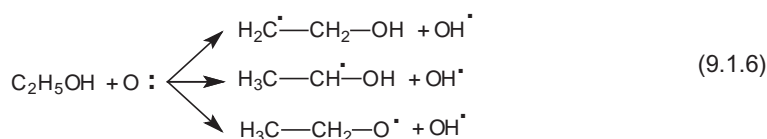


Reaction 9.1.4 has a unimolecular mechanism, and its rates are described by the expressions:  $k^\infty = 2.79 \times 10^{+13} T^{0.09} \exp(-33,284/T) \text{ s}^{-1}$  and  $k^0 = 2.57 \times 10^{+83} T^{-18.85} \exp(-43,509/T) (\text{cm}^3/\text{mol}/\text{s})$  [7]. The thermodynamic parameters of reactions 9.1.3 and 9.1.4 are not very different, which explains in part the occurrence of these reactions together. Acetaldehyde can further decompose with the formation of methane and CO by the reaction:



Various catalysts can influence the dominance of dehydrogenation or dehydration reactions during ethanol pyrolysis. For example, pyrolysis over  $\text{Al}_2\text{O}_3$  leads mainly to the formation of ethylene, while pyrolysis over reduced copper leads to the formation of acetaldehyde. A detailed study regarding the pyrolysis of ethanol in the presence of oxygen at various ethanol/oxygen ratios ( $\Phi = 0.7, 1.0, 1.5$ ) as well as in the absence of oxygen ( $\Phi = \infty$ ) and at temperatures between  $300^\circ\text{C}$  and  $1000^\circ\text{C}$  has been reported in the literature [1]. Besides the main pyrolysis products, which include  $\text{H}_2$ , acetaldehyde, water, and  $\text{CO}$ , other by-products were detected. These included acetone, formaldehyde, acetic acid, ethyl acetate, 2,3-butanediol, 3-hydroxy-2-butanone,  $\text{CO}_2$ , methane, ethane, ethylene, acetylene, and propylene. The variation in the relative level of main pyrolysis products of ethanol as a function of temperature in the absence of oxygen is given in Figure 9.1.2 (hydrogen not shown). The other pyrolysis products that are not shown in Figure 9.1.2 began to be generated around  $600^\circ\text{C}$ , had a maximum around  $700^\circ\text{C}$  of about  $10^{-3}$  from the initial level of ethanol, and practically disappeared at  $850^\circ\text{C}$ . Methane and ethane were seen only in the presence of oxygen ( $\Phi = 1.0$ ), while ethylene and acetylene were seen only in the absence of oxygen. The experiment for these results [1] was carried out in a quartz cylindrical flow reactor with a residence time of 2 s. The initial concentration of ethanol was 900 ppm.

Oxidative pyrolysis of ethanol has been the subject of numerous other studies performed mainly with the goal of understanding the behavior of ethanol as a fuel [7–13]. Complete combustion of ethanol with the formation of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  generates 310.7 kcal/mol. A complex set of reactions participates in the combustion process. The combustion starts with the formation of free radicals:



The free radicals continue with propagation reactions of the type:

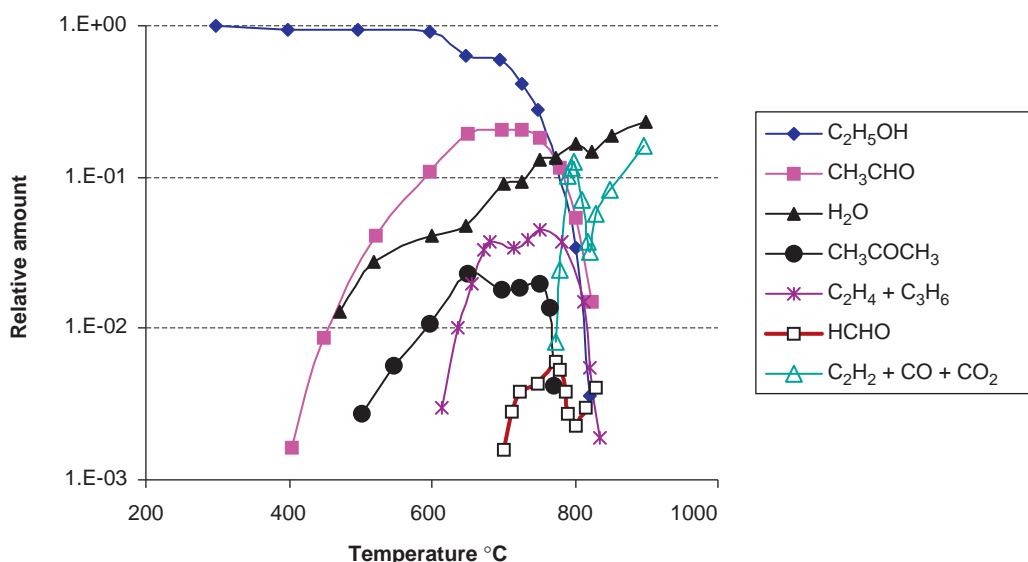
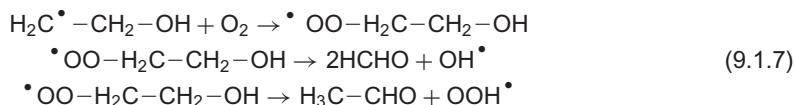


FIGURE 9.1.2. Relative distribution as a function of temperature of the main pyrolysis products for a sample of  $\text{C}_2\text{H}_5\text{OH}$  with initial concentration 900 ppm (smooth interpolation of data) at 2 s residence time in a flow experiment ( $\Phi = \infty$ ). The variation in the level of hydrogen is not shown [1].



Formaldehyde and acetaldehyde generate CO, CO<sub>2</sub>, and H<sub>2</sub>O in several reaction steps also involving peroxides formation. A kinetic model for ethanol combustion involving 372 reactions has been developed and reported in the literature [7]. During combustion, about 8% of the initial ethanol was estimated to undergo elimination of water by reaction 9.1.4 [8]. Ethylene that further pyrolyzes to acetylene is the only potential precursor for PAHs formation in ethanol combustion. Although present in ethanol flames, PAHs are at considerably lower levels compared to their levels in the flames of hydrocarbons.

Besides the studies on pure ethanol combustion, considerable amount of work is reported regarding the combustion of different blends of ethanol with other fuels [14] and regarding the oxidation of ethanol over various catalysts [15,16].

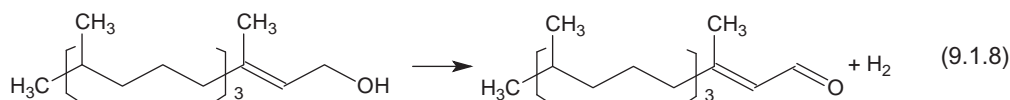
*n*-Propyl alcohol pyrolysis products are analogous to those of ethanol, the two dominating reactions during pyrolysis around 550–600 °C being propionaldehyde (as a result of dehydrogenation) and propene (as a result of water elimination). Different from ethanol pyrolysis is the fact that, depending on temperature, further decomposition reactions are noticed including the decomposition of propionaldehyde into CO and C<sub>2</sub>H<sub>6</sub> and the formation of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> from propene, from ethene, or even directly from the parent compound. Formation of traces of HCHO by the decomposition of *n*-propanol in this compound and in ethane is noticed also. Similarly, by pyrolysis butyl alcohol forms the corresponding aldehyde and the alkene. Among the compounds at low level in the pyrolysate are smaller alkenes, acetylene, and butadiene. An extensive study on butanol burning in premixed flames is reported in the literature [17].

### Other monohydroxy primary alcohols

As the hydrocarbon chain of an aliphatic alcohol extends, the main products of pyrolysis remain the corresponding aldehyde and the alkene. Some further fragmentation of the initial pyrolysis products leads to the formation of other compounds, mainly shorter alkenes. For example, pyrolysis of 1-decanol at 900 °C in a flash pyrolysis experiment generates decanal as a main pyrolysis product, with lower levels of 1-decene. Lower levels of other alkenes (C<sub>2</sub>–C<sub>9</sub>) as well as 1,3-butadiene and acetaldehyde were detected in the pyrolysate. Traces of toluene and styrene were detected also. Branched primary saturated alcohols behave similarly to the linear compounds, but typically more by-products of pyrolysis are generated.

For alcohols with more complex molecules, the reactions of the type 9.1.3 and 9.1.4 (H<sub>2</sub> elimination or H<sub>2</sub>O elimination), although likely to be the primary pyrolytic reactions, start to play a less-important role for final composition of the pyrolysates. The secondary reactions that act on the structure of the rest of the molecule or on the products of the initial reactions begin to play a more important role. One such example is pyrolysis of phytol (2*E*,7*R*,11*R*)-3,7,11,15-tetramethyl-2-hexadecen-1-ol (MW = 296.53 a.u.), with the pyrogram shown in Figure 9.1.3. Pyrolysis was performed on 0.60 mg compound using Type 1 Experiment as described in Section 4.6, at *T*<sub>eq</sub> = 900 °C, β = 10 °C/ms, THT = 10 s, and housing temperature *T*<sub>hou</sub> = 280 °C. The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications in the pyrogram and their relative molar content in 100 moles of pyrolysate are given in Table 9.1.1. The calculation of the mole % was obtained based solely on peak areas, and since differences in the MS response factors can be quite large, the estimations may have large errors.

As shown in Table 9.1.1, almost 50% (mol) of the phytol does not decompose in the experimental conditions selected for the pyrolysis. This is probably caused by the evaporation of phytol before it reaches the decomposition temperature and its rapid transfer into the GC/MS system. For phytol, the reaction occurring with hydrogen elimination and formation of (2*E*)-3,7,11,15-tetramethylhexadec-2-enal as expected for an alcohol does take place, but the compound is present in the pyrolysate at only 0.2% (mol) from the total pyrolysate composition. The reaction is shown below:



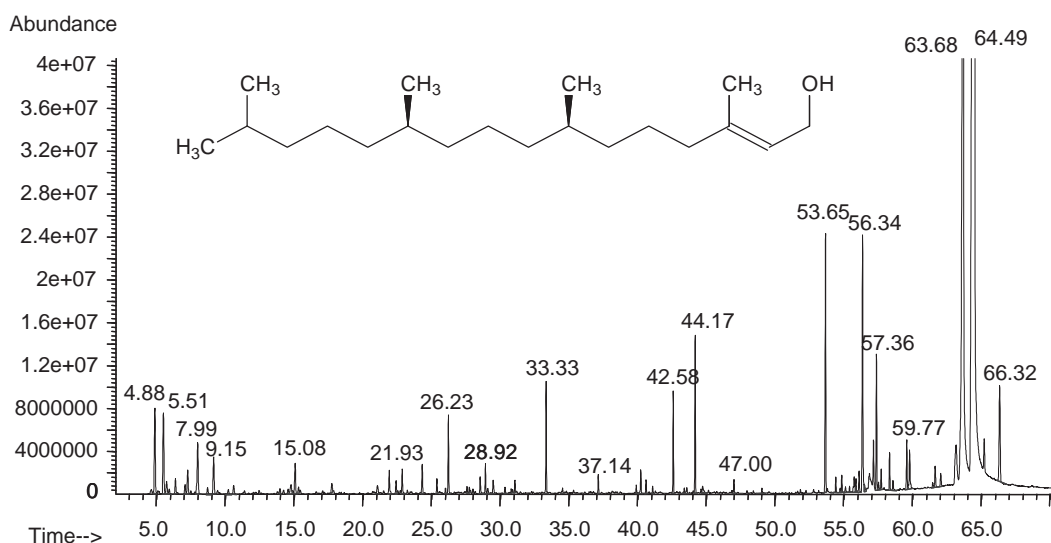


FIGURE 9.1.3. Pyrogram of phytol at 900 °C. Peak assignment is given in Table 9.1.1.

Elimination of water is unlikely without rearrangement of the double bond from the 2-position. In the case of phytol, most pyrolysis products are various fragments of phytol molecule from along the hydrocarbon chain. The levels of PAHs generated during phytol pyrolysis are negligible. Pyrolysis products are more similar to those of a long-chain hydrocarbon than those of a typical alcohol. This is common for a large molecule where the functional group is only a small part of a much larger structure.

Another example of a large molecule where the molecular backbone is more important than the functional group is solanesol (3,7,11,15,19,23,27,31,35-nonamethylhexa-triaconta-2,6,10,14,18,22,26,30,34-nonaen-1-ol)  $C_{45}H_{74}O$ . The compound is found in plants from Solanaceae family, such as tobacco, tomato, potato, and eggplant. The molecular structure of solanesol is rather similar to that of squalene (see Section 7.4), and the compound can be considered a polyterpene derivative. Results for pyrolysis of a solanesol sample are shown in Figure 9.1.4. The pyrolysis was performed on 0.20 mg material using Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900\text{ }^{\circ}\text{C}$ ,  $\beta = 10\text{ }^{\circ}\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280\text{ }^{\circ}\text{C}$ . The pyrolysate was analyzed under conditions given in Table 4.6.1. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 9.1.2. The calculation of the mole % was obtained based solely on peak areas.

As shown in Figure 9.1.4 and Table 9.1.2, the pyrolysis products of solanesol are very similar to those of squalene (see Figure 7.4.2 and Table 7.4.1; a difference of about 0.2 min in the retention time for identical compounds in the chromatograms of squalene and of solanesol are due to small variations in the experimental setup). Solanesol and squalene have a very similar hydrocarbon backbone, and the pyrolysis mechanism is very likely the same. Similar to the case of squalene, a relatively large proportion of cyclic and aromatic compounds can be seen in the pyrolysate of solanesol. This indicates that some levels of PAHs are likely to be generated during the pyrolysis of this compound. The pyrolysate also contains various fragments of the molecular backbone, and very little indication of the presence of the OH group is seen. The formation of 3-methyl-2-butenal is the only hint that a dehydrogenation process of solanesol may take place in addition to water elimination and fragmentation of the carbon chain. Solanesol being a large molecule, some nonvolatile fragments with more than 25–28 carbon atoms in the molecule also may be formed. However, the analysis conditions of the pyrolysate (the GC/MS experimental setup) do not allow the detection of such fragments that are not volatile. Since solanesol is present in tobacco leaves, it has been estimated that about 10% of the PAHs from cigarette smoke are generated from solanesol pyrolysis [18].

Benzyl alcohol or phenylmethan-1-ol is another common primary alcohol. A specific reaction occurs during pyrolysis of this compound. Beside toluene and benzaldehyde, which are expected pyrolysis

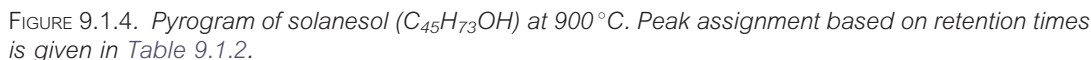
TABLE 9.1.1. Identification of the main peaks in the chromatogram shown in Figure 9.1.3 for the pyrolysis of phytol (hydrogen, CO, CO<sub>2</sub>, methane, ethane, and water are not included)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Propene	4.88	42	115-07-1	7.17
2	Formaldehyde	5.10	30	50-00-0	0.09
3	Isobutane	5.20	58	75-28-5	0.02
4	1-Butene	5.51	56	106-98-9	5.12
5	1,3-Butadiene	5.74	54	106-99-0	0.97
6	2-Butene	5.93	56	107-01-7	0.30
7	3-Methyl-2-butene	6.38	70	563-45-1	0.72
8	1-Pentene	7.08	70	109-67-1	0.50
9	3-Methyl-1-butene	7.27	70	563-45-1	1.19
10	1,2-Dimethylcyclopropane	7.5	70	930-18-7	0.17
11	2-Methyl-1,3-butadiene (isoprene)	7.99	68	78-79-5	3.05
12	1,3-Pentadiene	8.72	68	504-60-9	0.31
13	4-Methyl-1-pentene	9.16	84	691-37-2	1.64
14	Cyclopentadiene	9.44	66	542-92-7	0.18
15	2-Methyl-1,4-pentadiene	10.23	82	763-30-4	0.22
16	1-Hexene	10.62	84	592-41-6	0.38
17	4-Methyl-2-pentene	11.40	84	691-38-3	0.24
18	3-Methyl-1,3-pentadiene ( <i>E</i> )	12.47	82	2787-43-1	0.14
19	2,3-Dimethyl-1-pentene	13.80	98	2213-32-3	0.11
20	3-Methyl-1-hexene	13.98	98	3404-61-3	0.20
21	4-Methyl-1,3-pentadiene	14.25	82	926-56-7	0.22
22	1-Methylcyclopentene	14.57	82	693-89-0	0.24
23	1-Methyl-1,3-cyclopentadiene	14.78	80	96-39-9	0.57
24	4-Methyl-1-hexene	15.08	98	3769-23-1	1.18
25	3-Methylenecyclopentene	15.33	80	930-26-7	0.33
26	5-Methyl-1,3-cyclopentadiene	15.47	80	96-38-8	0.17
27	2-Methyl-1,5-hexadiene	16.62	96	4049-81-4	0.10
28	1,3-Cyclohexadiene	17.09	80	592-57-4	0.11
29	Benzene	17.75	78	71-43-2	0.58
30	4-Methyl-1,4-hexadiene	17.88	96	1116-90-1	0.12
31	5-Methyl-1,4-hexadiene	20.73	96	763-88-2	0.13
32	4-Methyl-1-heptene	21.07	112	13151-05-8	0.37
33	3-Methyl-1,3,5-hexatriene ( <i>Z</i> )	21.51	94	24587-27-7	0.15
34	6-Methyl-2-heptene	21.93	112	73548-72-8	0.67
35	2-Methyl-3-heptene	22.42	112	17618-76-7	0.33
36	3-Methylcyclohexene	22.55	96	591-48-0	0.12
37	1,3-Cycloheptadiene?	22.73	94	4054-38-0	0.14
38	2-Methyl-1-heptene	22.87	112	15870-10-7	0.69
39	1-Methyl-1,4-cyclohexadiene	23.24	94	4313-57-9	0.14
40	Toluene	24.32	92	108-88-3	0.88
41	1,3-Dimethylcyclohexene	25.40	110	2808-76-6	0.38
42	3-Methyl-1-octene	26.02	126	13151-08-1	0.12
43	2,6-Dimethyl-1-heptene	26.23	126	3074-78-0	1.56

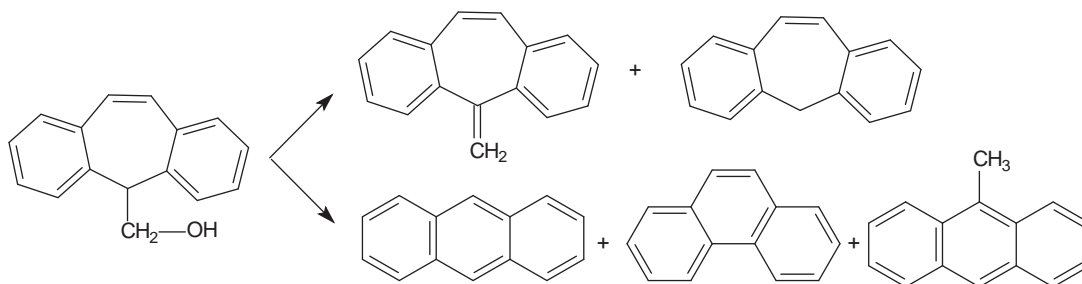
TABLE 9.1.1. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
44	4-Nonene?	27.58	126	2198-23-4	0.15
45	1,3-Dimethyl-2-methylene- <i>cis</i> -cyclohexane	27.84	124	19781-47-6	0.07
46	1,2,3-Trimethylcyclohexane	28.01	126	1678-97-3	0.11
47	2-Methyl-3-butenol	28.54	84	107-86-8	0.56
48	3,7-Dimethyl-1-octene	28.93	140	1/4/4984	0.53
49	Ethylbenzene	29.09	106	100-41-4	0.17
50	1,3-Dimethylbenzene ( <i>m</i> -xylene)	29.48	106	108-38-3	0.41
51	2-Undecene?	30.35	152	60212-29-5	0.11
52	1,4-Dimethylbenzene ( <i>p</i> -xylene)	30.80	106	106-42-3	0.11
53	2,6-Dimethyl-1-octene	31.07	140	6874-29-9	0.19
54	4-Methyl-1-decene	33.33	154	13151-29-6	1.67
55	4-Methyl-1-undecene	37.14	168	74630-39-0	0.25
56	2,5-Dimethyl-2-undecene	40.23	182	49622-16-4	0.32
57	7-Methyl-6-tridecene	42.58	196	24949-42-6	1.12
58	1-Pentadecene?	44.18	210	13360-61-7	1.71
59	3-Teradecene?	44.60	196	41446-68-8	0.04
60	2,6,10-Trimethyldodecane	47.00	212	3891-98-3	0.15
61	3,7,11,15-Tetramethyl-2-pentene	53.66	266	N/A	2.50
62	Phytol fragment	54.40	278	N/A	0.13
63	3,7,11,15-Tetramethyl-2-hexadecene	54.83	280	14237-73-1	0.16
64	Phytol fragment	55.74	278	N/A	0.21
65	3,7,11,15-Tetramethyl-2-hexadecene isomer	55.87	280	N/A	0.12
66	3,7,11,15-Tetramethyl-2-hexadecene isomer	56.09	280	N/A	0.20
67	2-(4,8,12-Trimethyltridecyl)-1,3-butadiene neophytadiene	56.34	278	504-96-1	2.65
68	3,7,11,15-Tetramethyl-2-hexadecen-1-ol isomer?	56.85	296	102608-53-7	0.51
69	Eicosadiene	57.14	278	N/A	0.54
70	1,4-Eicosadiene	57.36	278	1000131-16-3	1.17
71	(2 <i>E</i> )-3,7,11,15-Tetramethylhexadec-2-enal	57.50	294	N/A	0.20
72	6,10,14-Trimethyl-2-pentadecanone	58.32	268	502-69-2	0.37
73	6,10,14-Trimethyl-2-pentadecanone isomer	59.56	268		0.50
74	Isophytol?	59.77	296	505-32-8	0.47
75	Phytol type?	61.63	252		0.28
76	3,7,11,15-Tetramethyl-1-hexadecanol	63.14	298	645-72-7	0.95
77	(2 <i>E</i> )-3,7,11,15-Tetramethyl-2-hexadecen-1-ol (phytol)	63.68	296	150-86-7	<b>16.84</b>
78	(2 <i>Z</i> )-Phytol	64.49	296	150-86-7	<b>30.72</b>
79	Unknown	65.21	296	N/A	0.64
80	Unknown	66.32	296	N/A	1.15

Note: Bold numbers in this and subsequent tables indicate main pyrolysis products.


$$2 \text{ C}_6\text{H}_5\text{CH}_2\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{C}_6\text{H}_5 \quad (9.1.9)$$

Pyrolysis of other primary alcohols with simple or with more complicated structures is reported in the literature. Depending on individual compound structure, the thermal decomposition reactions may follow a typical scheme for alcohols or may generate compounds due to different reaction paths. This can be exemplified by the pyrolysis of an annulene alcohol 5-hydroxymethyl-5H-dibenzo[*b,f*]cycloheptene [20]. The compounds generated by pyrolysis of this alcohol are shown as follows:



The 5-methylenedibenzo[a,d][7]annulene results from a typical water elimination of alcohols. The formation of 5-hydrodibenzo[a,d][7]annulene is explained easily by the fragmentation of the bond between the CH<sub>2</sub>OH group and the C atom with sp<sup>3</sup> hybridization in the cycloheptene cycle (this type of

TABLE 9.1.2. Identification of the main peaks in the chromatogram shown in Figure 9.1.4 for the pyrolysis of solanesol (hydrogen, methane, ethylene, and water were not analyzed due to the mass spectrometer settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Propene	4.84	42	115-07-1	3.09
2	2-Methyl-1-propene	5.47	56	115-11-7	2.94
3	1,3-Butadiene	5.70	54	106-99-0	0.34
4	3-Methyl-1-butene	6.34	70	563-45-1	1.15
5	2-Methyl-1-butene	7.25	70	563-46-2	1.38
6	2-Methyl-2-butene	7.93	70	513-35-9	<b>37.31</b>
7	4-Methyl-2-pentene	9.51	84	691-38-3	0.22
8	2-Methyl-2-pentene	11.37	84	625-27-4	1.13
9	3-Methyl-2-pentene (Z)	11.68	84	922-62-3	0.22
10	3-Methyl-2-pentene (E)	12.19	84	616-12-6	0.46
11	2,4-Hexadiene (E,E)	14.22	82	5194-51-4	0.75
12	1-Methyl-1,3-cyclopentadiene	14.74	80	96-39-9	1.62
13	5-Methyl-1,3-cyclopentadiene	15.30	80	96-38-8	1.19
14	2,4-Hexadiene (Z,Z)	15.44	82	6108-61-8	0.58
15	3-Methylenecyclopentene	17.45	80	930-26-7	0.59
16	Benzene	17.74	78	71-43-2	0.99
17	1,3,5-Heptatriene	20.75	94	17679-93-5	0.19
18	2,5-Dimethyl-2-hexene	21.22	112	3404-78-2	0.43
19	1-Methyl-1,4-cyclohexadiene	21.49	94	4313-57-9	0.82
20	5,5-Dimethyl-1,3-cyclopentadiene	21.85	94	4125-18-2	0.28
21	3-Methyl-1,3,5-hexatriene	22.00	94	24587-27-7	0.54
22	3-Methylenecyclohexene	22.50	94	1888-90-0	0.54
23	2-Methyl-1,3,5-hexatriene	22.72	94	19264-50-7	0.48
24	1,2-Dimethyl-1,3-cyclopentadiene	23.22	94	4784-86-5	0.70
25	1,3-Cycloheptadiene	23.42	94	4054-38-0	0.47
26	Toluene	24.30	92	108-88-3	3.99
27	3-Methyl-2-buten-1-ol	27.42	86	556-82-1	0.47
28	2,3-Dimethylcyclohexa-1,3-diene	27.71	108	4430-91-5	0.48
29	2,6-Dimethyl-1,5-heptadiene	28.15	124	6709-39-3	0.88
30	3-methyl-2-butenal	28.52	84	107-86-8	0.72
31	1,6-Dimethylhepta-1,3,5-triene	28.90	122	N/A	1.71
32	2,6-Dimethyl-2,6-octadiene (6Z)	28.98	138	2492-22-0	0.44
33	1,3-Dimethylbenzene ( <i>m</i> -xylene)	29.46	106	108-38-3	<b>6.53</b>
34	1,3,5,5-Tetramethyl-1,3-cyclohexadiene	30.27	136	4724-89-4	0.26
35	2,3,6-Trimethyl-1,5-heptadiene	30.58	138	33501-88-1	0.48
36	1,4-Dimethylbenzene ( <i>p</i> -xylene)	30.77	106	106-42-3	0.98
37	Styrene	31.15	104	100-42-5	0.59
38	5,5-Dimethyl-2-propyl-1,3-cyclopentadiene?	31.90	136	N/A	0.38
39	4-Ethenyl-1,4-dimethyl-cyclohexene	32.03	136	1743-61-9	1.93
40	2,6-Dimethyl-2- <i>trans</i> -6-octadiene	32.51	138	2609-23-6	0.58

(Continued)

TABLE 9.1.2. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
41	2,7-Dimethyl-1,6-octadiene	32.64	138	40195-09-3	2.37
42	3,3,5-Trimethyl-1,5-heptadiene	32.98	138	74630-29-8	1.39
43	1-Methyl-4-(1-methylethylidene)cyclohexene	33.17	136	586-62-9	0.84
44	1-Ethyl-3-methylbenzene	33.27	120	620-14-4	0.90
45	1-Ethyl-2-methylbenzene	33.39	120	611-14-3	0.37
46	1,2,3-Trimethylbenzene	33.57	120	526-73-8	0.66
47	2,5,6-Trimethyl-1,3,6-heptatriene	34.08	136	42123-66-0	0.91
48	1-Methyl-4-(1-methylethyl)-cyclohexene	34.51	138	1195-31-9	0.91
49	2,5-Dimethyl-3-methylene-1,5-heptadiene	34.70	136	74663-83-5	0.48
50	1,3,5-Trimethylbenzene	34.78	120	108-67-8	1.48
51	1-Methyl-4-(1-methylethenyl)-cyclohexene (limonene)	35.01	136	138-86-3	<b>7.80</b>
52	1-Ethenyl-4-methylbenzene	35.30	118	622-97-9	0.64
53	3,7-Dimethyl-1,3,6-octatriene	35.52	136	3338-55-4	0.74
54	5,7-Dimethyl-1,6-octadiene	36.02	138	85006-04-8	0.21
55	1,2,4-Trimethylbenzene	36.12	120	95-63-6	0.52
56	1-Methyl-4-(1-methylethenyl)benzene	38.43	132	1195-32-0	0.46
57	1-Ethyl-3,5-dimethylbenzene	39.37	134	934-74-7	0.32
58	Unknown	43.77	190	N/A	0.09
59	7-Isopropenyl-4a-methyl-1-methylenedeca-hydronaphthalene (eudesma-4(14),11-diene)?	47.28	204	N/A	0.10

C–C fragmentation is seen in many other alcohols (see reaction 9.1.17). On the other hand, the formation of anthracene, phenanthrene, and 9-methylantracene is explained by a reaction of the type 2.4.6 showing the elimination of a group from dibenzoannulenes (see Section 2.4).

### Vitamin A

Alcohol groups frequently are present in more complex molecules. For example, vitamin A, also known as retinol or 3,7-dimethyl-9-(2,6,6-trimethyl-1-cyclohexenyl)nona-2,4,6,8-tetraen-1-ol, is a primary alcohol with important biological functions. The compound is related to other biologically active molecules such as retinal, retinoic acid, and  $\beta$ -carotene. Retinol is not a stable molecule; even *trans* and *cis* configurations of retinol change easily, which is important for its biological activity. Retinol pyrolysis generates numerous fragments as shown in Figure 9.1.5, which displays the pyrogram obtained from 1 mg retinol. The pyrolysis was performed using Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ . The pyrolysate was analyzed under conditions given in Table 4.6.1. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 9.1.3. Calculation of the mole % was based solely on peak areas.

Many pyrolysis products of retinol are similar to those of  $\beta$ -carotene (formed from two retinyl groups) (see Section 7.5). Retinol being a large molecule, its pyrolysis products are dominated by fragments of the retinyl group. The main initial reactions during pyrolysis of retinol are likely the elimination of water and of  $\text{H}_2$ , typical processes for alcohols.

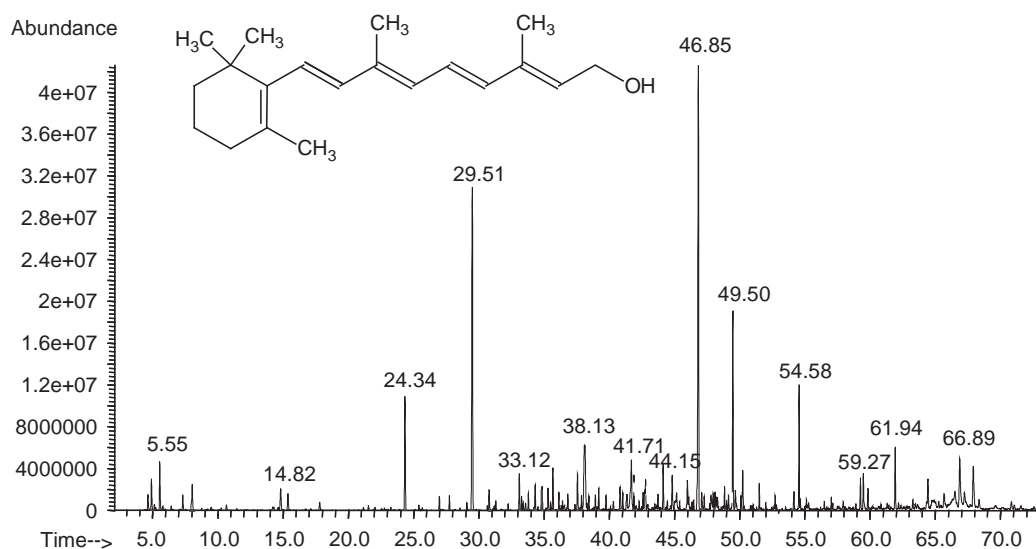
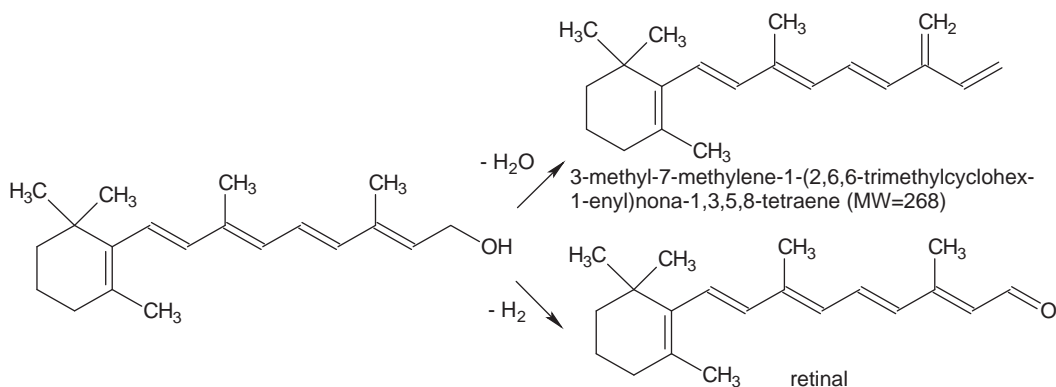


FIGURE 9.1.5. Pyrogram of retinol ( $C_{20}H_{29}OH$ ,  $MW = 286$ ) at  $900^{\circ}C$ . Peak assignment is given in Table 9.1.3.



As shown in Table 9.1.3, no retinal ( $MW = 284$ ) was detected in the pyrolysate, possibly due to its rapid decomposition. However, several compounds with the  $MW = 268$  were present. Starting, for example, with 3-methyl-7-methylene-1-(2,6,6-trimethylcyclohex-1-enyl)nona-1,3,5,8-tetraene, it can be seen how further reactions lead to smaller fragments, such as compounds with  $MW = 240$ , which also were detected in the pyrolysate:

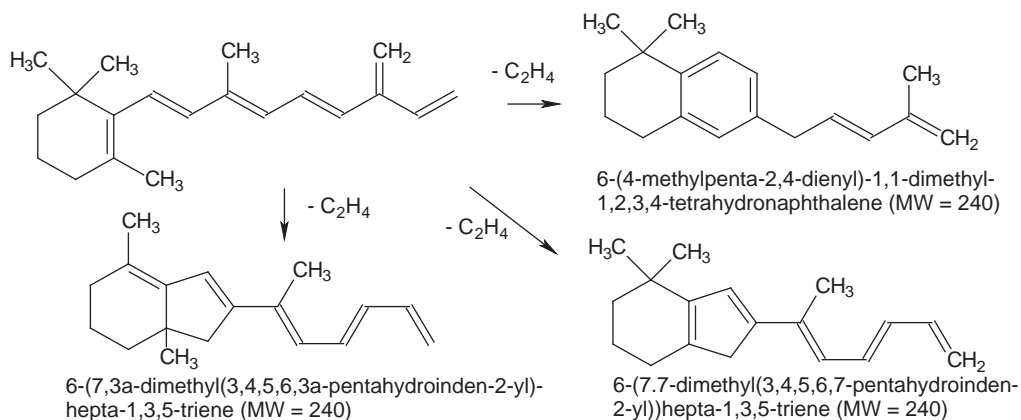




TABLE 9.1.3. Identification of the main peaks in the chromatogram shown in Figure 9.1.5 for the pyrolysis of retinol (hydrogen, methane, ethylene, and water were not analyzed due to the mass spectrometer settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Propene	4.92	42	115-07-1	3.96
2	2Methyl-1-propene	5.55	56	115-11-7	4.57
3	2-Methyl-1,3-butadiene (isoprene)	8.04	68	78-79-5	2.74
4	1-Methyl-1,3-cyclopentadiene	14.82	80	96-39-9	1.94
5	Benzene	17.80	78	71-43-2	0.58
6	Toluene	24.34	92	108-88-3	<b>6.79</b>
7	1,3-Dimethylbenzene ( <i>m</i> -xylene)	29.51	106	108-38-3	<b>20.31</b>
8	1,4-Dimethylbenzene ( <i>p</i> -xylene)	30.80	106	106-42-3	1.00
9	1,2,3,4,5-Pentamethylcyclopentene?	33.12	138	N/A	1.17
10	3,3-Dimethyl-6-methylenecyclohexene	34.33	122	20185-16-4	1.03
11	1,3,5-Trimethylbenzene	34.82	120	108-67-8	0.79
12	1-Ethenyl-4-methylbenzene	35.32	118	622-97-9	0.88
13	1-Vinyl-2,6,6-trimethylcyclohex-1-ene	35.69	150	5293-90-3	1.24
14	1,2,4-Trimethylbenzene	36.15	120	95-63-6	0.63
15	1-Vinyl-2,6,6-trimethylcyclohex-1-ene isomer	37.58	150	N/A	1.18
16	1-Ethyl-3-(1-methylethyl)benzene	38.13	148	4920-99-4	<b>5.66</b>
17	1-Ethyl-4-(1-methylethyl)benzene	39.21	148	4218-48-8	0.62
18	1,2,4-Trimethyl-1-(1-methylethyl)benzene	40.84	162	33991-29-6	0.77
19	1-(Prop-1-enyl)-2,6,6-trimethylcyclohexadiene or isomer	41.71	162	N/A	2.81
20	1-(But-1-enyl)-2,6,6-trimethylcyclohex-1-ene or isomer	41.91	178	N/A	0.88
21	4-Methylphenol	42.61	108	106-44-5	0.76
22	3-Methyl-1-(2,6,6-trimethylcyclohex-1-enyl)buta-1,3-diene	42.80	190	N/A	0.79
23	1,1,4-Trimethyl-2,3-dihydro-1H-indene	44.15	160	16204-72-1	1.38
24	3-Methyl-1-(2,6,6-trimethylcyclohex-1-enyl)buta-1,3-diene isomer	44.85	190	N/A	1.14
25	Unknown	46.01	136	N/A	0.91
26	1,1,6-Trimethyl-1,2,3,4-tetrahydronaphthalene	46.85	174	475-03-6	<b>17.24</b>
27	1,2-Dihydro-1,1,6-trimethylnaphthalene	47.11	172	30364-38-6	0.52
28	1,2,3-Trimethyl-1H-lindene	48.13	158	4773-83-5	0.48
29	3-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-2-propen-1-ol	49.50	180	4808-01-9	5.53
30	2,6-Dimethylnaphthalene	49.68	156	581-42-0	0.60
31	1,7-Dimethylnaphthalene	50.26	156	575-37-1	1.54

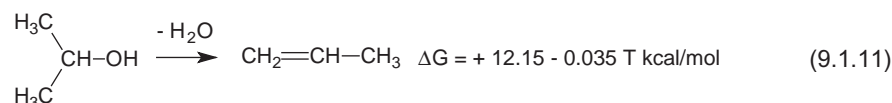
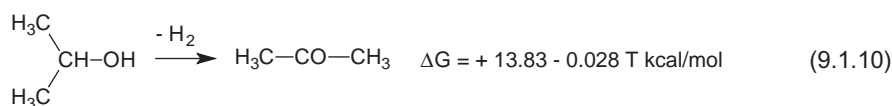
TABLE 9.1.3. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
32	2-(2-Methylpenta-1,3-dienyl)-7,7-dimethyl-3,4,5,6,7-pentahydroindene	51.52	228	N/A	0.47
33	3,7-Dimethyl-1-(2,6,6-trimethylcyclohex-1-enyl)octa-1,3,5-triene (retinol fragment)	54.19	258	N/A	0.40
34	Retinol fragment (with no OH)	54.58	260	N/A	2.08
35	Retinol fragment with aromatic ring (with no OH)	59.27	240	N/A	0.61
36	Retinol fragment (with no OH)	59.50	268	N/A	0.72
37	Retinol fragment (with no OH)	59.86	268	N/A	0.39
38	Retinol fragment with aromatic ring (with no OH)	61.94	240	N/A	1.33
39	Retinol fragment with aromatic ring (with no OH)	64.45	238	N/A	0.75
40	Retinol isomer?	66.89	286	N/A	1.53
41	3,7-Dimethyl-9-(2,6,6-trimethyl-1-cyclohexenyl)nona-2,4,6,8-tetraen-1-ol (retinol)	67.92	286	68-26-8	1.28

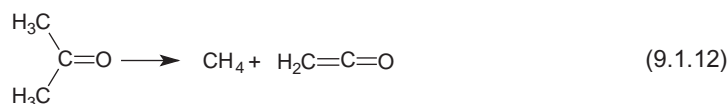
Further decompositions lead to the formation of even smaller molecules, some reactions occurring with hydrogen elimination and formation of aromatic compounds such as toluene (6.8%), *m*-xylene (20.3%), and 1-ethyl-3-(1-methylethyl)benzene (5.7%).

### Monohydroxy secondary and tertiary alcohols

The main thermal decomposition reactions for isopropyl alcohol are similar to those for primary alcohols. Around 615 °C there are two dominant reactions, one leading to acetone and the other to propene, shown as follows:

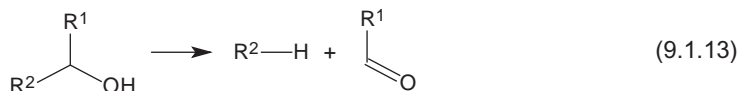


However, other pyrolysis products are generated from isopropanol, including acetaldehyde, CO, CH<sub>4</sub>, butene, and butadiene. These compounds are generated by various other reactions involving either the parent molecule or the products of the first step reactions. Acetone for example (see Section 15.2) can further decompose to generate CH<sub>4</sub> and ketene:



One other potential route for methane formation is the direct dissociation of isopropanol with the generation of CH<sub>3</sub>• free radicals, followed by further hydrogen transfer reactions. The same dissociation

may be the source of acetaldehyde. Acetaldehyde can be generated from the reduction of ketene when hydrogen is present. The formation of acetaldehyde also is possible following the general reaction:



For the case of isopropanol, this reaction also can account for the formation of methane. The reaction is not uncommon for other secondary alcohols.

Another example of a secondary alcohol is menthol, 5-methyl-2-(methylethyl)-cyclohexan-1-ol. This molecule has a cyclic hydrocarbon backbone and contains three asymmetric carbons. In nature, the common molecule of (–)-menthol has a (1*R*,2*S*,5*R*) configuration. As an example, the pyrogram of (–)-menthol is given in Figure 9.1.6. Pyrolysis was performed on 0.50 mg compound using Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ . The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications in the pyrogram and their relative molar content in 100 moles of pyrolysate are given in Table 9.1.4. The calculation of the mole % was obtained based solely on peak areas.

As shown in Figure 9.1.6 and Table 9.1.4, the main decomposition products of menthol are propene, *p*-menth-3-ene, *p*-menth-2-ene, benzene, and toluene. *p*-Menth-3-ene, and *p*-menth-2-ene are generated by the elimination of one molecule of water from the menthol, in a reaction similar to 9.1.11. On the other hand, the formation of menthone (as a result of a reaction similar to 9.1.10) is not a major outcome of pyrolysis. Some menthone is probably generated during pyrolysis but the formation of this compound was difficult to prove since the parent menthol molecule contained a trace of menthone as an impurity.

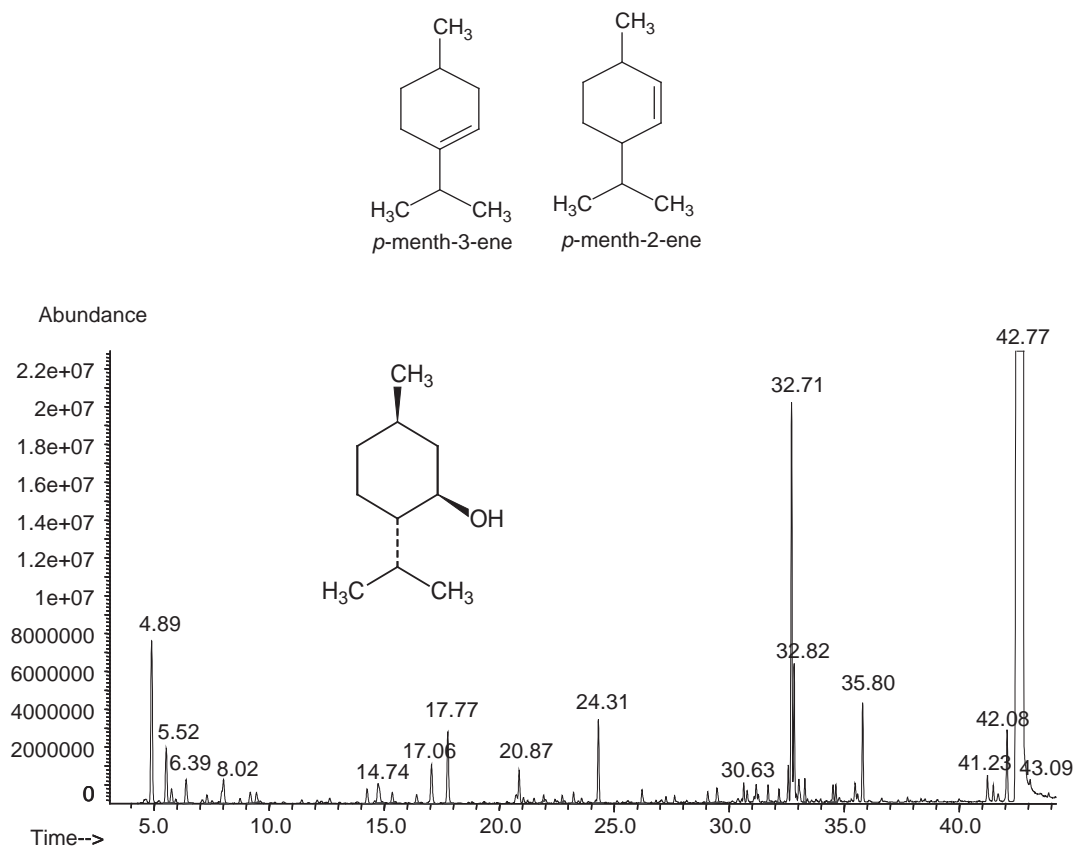


FIGURE 9.1.6. Pyrogram of menthol ( $\text{C}_{10}\text{H}_{19}\text{OH}$ ) at  $900^\circ\text{C}$ . Peak assignment is given in Table 9.1.4.

TABLE 9.1.4. Identification of the main peaks in the chromatogram shown in Figure 9.1.6 for the pyrolysis of menthol (hydrogen, methane, ethylene, and water were not analyzed due to the mass spectrometer settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Propene	4.89	42	115-07-1	<b>7.84</b>
2	Isobutene	5.20	58	75-28-5	0.12
3	2-Methyl-1-propene	5.52	56	115-11-7	1.95
4	1,3-Butadiene	5.76	54	106-99-0	0.55
5	2-Butene	5.93	56	107-01-7	0.12
6	2-Methyl-1-butene	6.39	70	563-46-2	0.73
7	3-Methyl-1-butene	7.30	70	563-45-1	0.25
8	1,2-Pentadiene	8.02	68	591-95-7	1.02
9	2-Methyl-1,3-butadiene	8.74	68	78-79-5	0.15
10	4-Methyl-1-pentene	9.18	84	691-37-2	0.30
11	1,3-Cyclopentadiene	9.45	66	542-92-7	0.32
12	2-Methyl-1,3-pentadiene	12.63	82	926-54-5	0.12
13	2,4-Hexadiene (Z,Z)	14.26	82	6108-61-8	0.36
14	3-Methyl-1,3-pentadiene	14.74	82	2787-43-1	0.80
15	1-Methyl-1,3-cyclopentadiene	15.35	80	96-39-9	0.25
16	2-Methyl-1,4-hexadiene	16.41	96	1119-14-8	0.19
17	5-Methyl-1,3-cyclopentadiene	17.06	80	96-38-8	1.09
18	Benzene	17.77	78	71-43-2	1.85
19	3-Ethenylcyclopentene	20.74	94	26727-45-7	0.23
20	4-Methylcyclohexene	20.87	96	591-47-9	0.62
21	6-Methyl-1-heptene	21.05	112	5026-76-6	0.10
22	1,3,5-Heptatriene (E,E)	21.52	94	17679-93-5	0.10
23	6-Methyl-2-heptene	21.93	112	73548-72-8	0.07
24	2-Methyl-3-heptene	22.43	112	692-96-6	0.06
25	2-Methyl-1,3,5-hexatriene	22.74	94	19264-50-7	0.11
26	1-Methyl-1,4-cyclohexadiene	23.23	94	4313-57-9	0.21
27	2-Ethyl-butenal	23.58	98	19780-25-7	0.10
28	Toluene	24.31	92	108-88-3	1.49
29	2,6-Dimethyl-1-heptene	26.21	126	3074-78-0	0.17
30	2,6-Dimethyl-3-heptene	26.80	126	2738-18-3	0.05
31	1,3-Dimethyl-2(1-methylethyl)cyclopentene	27.25	138	61142-32-3	0.07
32	4-Methyl-3-penten-2-one	27.62	98	141-79-7	0.16
33	Ethylbenzene	29.06	106	100-41-4	0.17
34	1,3-Dimethylbenzene (m-xylene)	29.46	106	108-38-3	0.26
35	Carane (cis)	30.38	138	2778-68-9	0.07
36	Ethylidenecycloheptane?	30.63	124	10494-87-8	0.22
37	1,4-Dimethylbenzene (p-xylene)	30.78	106	106-42-3	0.19
38	3,3-Dimethyl-6-methylenecyclohexene	31.08	122	20185-16-4	0.08
39	Styrene	31.17	104	100-42-5	0.29
40	p-Menth-4-ene	31.26	138	1124-27-2	0.08
41	(1-Methylethyl)benzene	31.69	120	98-82-8	0.26

(Continued)

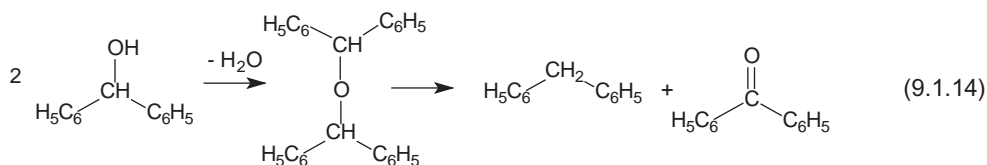
TABLE 9.1.4. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
42	(2-Methyl-2-propenyl)cyclohexane	32.16	138	3990-93-0	0.15
43	1-Methyl-3-(2-methyl-1-propenyl)cyclopentane	32.56	138	75873-01-7	0.36
44	<i>p</i> -Menth-3-ene	32.71	138	500-00-5	<b>4.15</b>
45	<i>p</i> -Menth-2-ene	32.82	138	5256-65-5	1.35
46	2,6-Dimethyl-1,3,6-heptatriene (3 <i>E</i> )	33.03	122	N/A	0.36
47	2,6-Dimethyl-1,3,6-heptatriene (3 <i>Z</i> )	33.29	122	928-67-6	0.26
48	1-Methyl-4-(1-methylethyl)cyclohexene	34.51	138	5502-88-5	0.19
49	3,7,7-Trimethylbicyclo[4.1.0]heptane	34.63	138	2778-68-9	0.16
50	1,2,4-Trimethylbenzene	34.79	120	95-63-6	0.08
51	6-Methylcyclohex-2-en-1-ol	35.47	112	N/A	0.29
52	1-Methyl-2-(1-methylethyl)benzene	35.58	134	527-84-4	0.09
53	3-Methylcyclohexanone	35.80	112	591-24-2	1.26
54	5-Methyl-3-(1-methylethyl)cyclohexene	36.63	136	8/1/5681	0.04
55	Borneol	41.23	154	10385-78-1	0.30
56	Isopulegol*	41.48	154	89-79-2	0.16
57	2-Octenol?	41.69	128	4798-61-2	0.13
58	Menthone*	42.08	154	10458-14-7	0.72
59	Menthol	42.77	156	1490-04-6	<b>66.40</b>
60	Isomenthol (from the parent compound)	43.09	156	N/A	0.39

\*Traces of isopulegol and of menthone were detected as impurities in the initial sample of menthol. These compounds were detected also in the pyrolysate where they may have been transferred from the initial sample or were generated by pyrolysis. The area ratios of the peaks of these compounds to the menthol peak were lower in the chromatogram of the menthol sample as compared to the pyrolysate. For this reason it was concluded that isopulegol and menthone were generated also by pyrolysis.

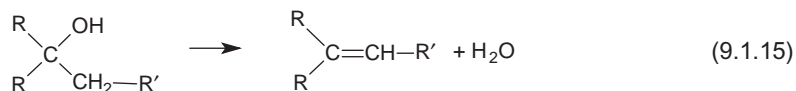
Propene as well as other fragments found in the pyrolysate are formed by C–C cleavages. The presence of relatively high levels of aromatic compounds such as benzene and toluene in the pyrolysate of menthol indicates the possibility of the formation of heavier aromatic hydrocarbons including PAHs. However, menthol added as an ingredient to tobacco for some cigarette brands is not a likely source of PAHs in cigarette smoke. Menthol, being volatile, is transferred from the tobacco to smoke by a distillation process [21] before reaching the temperatures necessary for decomposition. Experimental pyrolysis of menthol using a Type 3 Experiment as described in Section 4.6 with pyrolysis conditions similar to those described in Table 4.1.1 to mimic a burning cigarette, showed that over 99% of initial menthol is transferred during pyrolysis in intact form, with only 0.4% decomposed to menthene and 0.1% into menthone.

Among other secondary alcohols can be included diphenylmethanol (benzhydrol,  $\text{C}_6\text{H}_5\text{--CH(OH)--C}_6\text{H}_5$ ). The two main pyrolysis products of benzhydrol generated above 400 °C are benzophenone and diphenylmethane. It is likely that the pyrolysis generates first diphenylmethyl ether that further forms the two main pyrolysis products, as shown below:



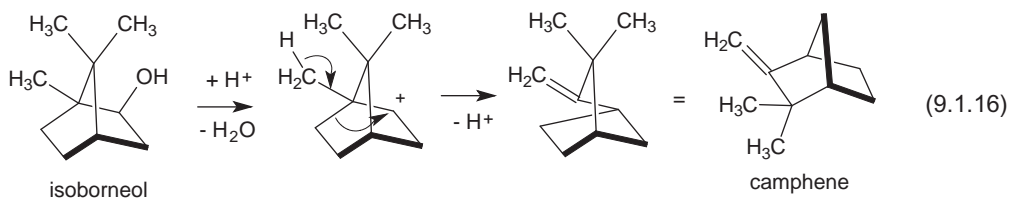
Other compounds detected in the pyrolysate at lower levels include styrene (at about 4% mol of pyrolysate), benzene (2%), benzaldehyde and triphenylmethane (1%), and toluene (0.25%).

Typical thermal decomposition of tertiary alcohols that have in the  $\beta$ -position to the OH group a carbon bearing hydrogen takes place with the formation of unsaturated hydrocarbons and water, as shown in the following reaction:

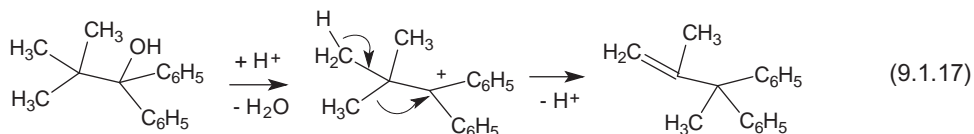


*Tert*-butyl alcohol (2-methylpropan-2-ol), for example, decomposes around 500 °C with the formation of 2-methylpropene and water. At higher temperatures above 600 °C, other reactions start to be noticed, with the formation of typical decomposition products of hydrocarbons including H<sub>2</sub>, shorter hydrocarbons, and char. In addition to these pyrolysate constituents, some CO is generated at higher temperatures, indicating that additional decomposition paths are initiated from the alcohol. A similar behavior is seen for other tertiary alcohols with structures similar to *tert*-butyl alcohol, the initial decomposition temperature with water elimination being dependent on the alcohol structure. The process is common not only for simple alcohols, but also for more complex molecules.

For secondary alcohols having no hydrogen on the  $\beta$ -carbon to the OH group, the dehydration reaction can take place by a mechanism similar to that of a Wagner–Meerwein rearrangement. A typical Wagner–Meerwein rearrangement takes place involving a carbocation formation in acidic conditions. The classical Wagner–Meerwein rearrangement of isoborneol to camphene is shown below:

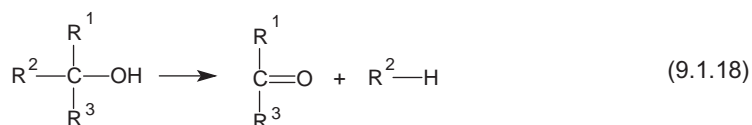


For a compound such as 2,2-dimethyl-1,1-diphenylpropan-1-ol where the  $\beta$ -carbons to the OH group are not bound to any hydrogens, the main result of the pyrolysis reaction is the formation of water and of 2-methyl-3,3-diphenyl-1-butene, as shown below:



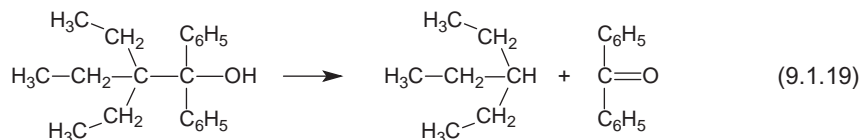
The carbocation formation in this reaction is not proven, but the slight acidity of the alcohol may provide the necessary protons for the mechanism shown in reaction 9.1.17.

A different type of reaction that is possible for tertiary alcohols when heated at temperatures around 450 °C takes place with the cleavage of the C–C bond involving the carbon to which the OH group is connected. This reaction leads to a fragmentation of the molecule as shown below:



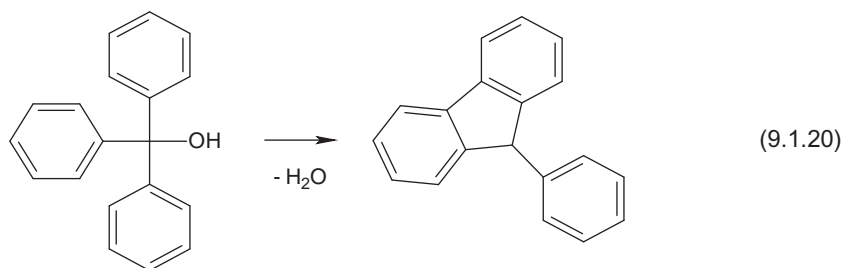
The reaction typically occurs for alcohols having no hydrogen on the  $\beta$ -carbons to the OH group, as shown below for 2,2-diethyl-1,1-diphenylbutan-1-ol, which generates 3-ethylpentane and diphenyl

ketone (benzophenone):



The overall molecular structure is important for the outcome of alcohols pyrolysis, and tertiary alcohols are not an exception to this rule. As previously indicated, the lack of hydrogen atoms on the  $\beta$ -carbon to the OH group makes the pyrolysis outcome less predictable. As an example, a time window from the pyrogram of triphenylmethanol ( $\alpha,\alpha$ -diphenylbenzenemethanol) is shown in Figure 9.1.7, and the identification of the peaks in the pyrogram based on their retention time is given in Table 9.1.5. Pyrolysis was performed on 0.40 mg compound using Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ . The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1.

Pyrolysis mechanism of triphenylmethanol shows some similarity to reactions 9.1.14 and 9.1.18. Benzophenone (generated by one or both of the two reactions) is present in the pyrolysate, but reactions such as water elimination involving hydrogens at C3 to the carbon bearing the OH group to form fluorene derivatives takes place with higher yield. The reaction for 9-phenyl-9H-fluorene formation is shown below:



Even some tertiary alcohols with hydrogen-containing alkyl groups bound to the carbon bearing the OH undergo fragmentation reactions by pyrolysis. A number of alcohols reported to undergo thermal

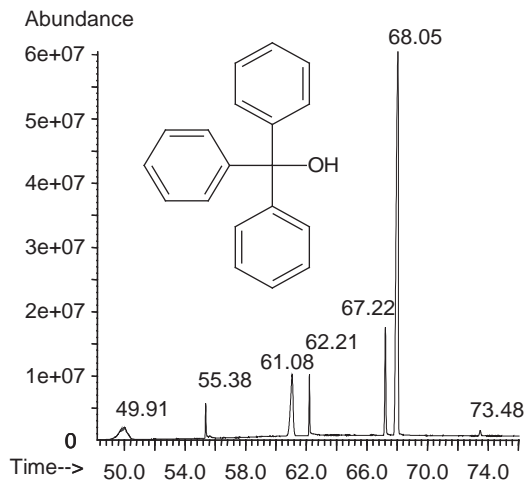


FIGURE 9.1.7. Pyrogram of triphenylmethanol. Peak assignment given in Table 9.1.5.

TABLE 9.1.5. Identification of the main peaks in the chromatogram shown in Figure 9.1.7 for the pyrolysis of triphenylmethanol

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Benzene	16.93	78	71-43-2	0.58
2	Phenol	38.83	94	108-95-2	0.24
3	1,1',1''-(1-Ethanyl-2-ylidene)-trisbenzene	49.94	258	1520-42-9	0.12
4	Benzophenone	55.38	182	119-61-9	3.16
5	(1,1,3,3-Tetraphenyl)methylether	61.09	350	N/A	10.79
6	Triphenylmethane	62.22	244	519-73-3	4.56
7	9-Phenyl-9H-fluorene	67.23	242	789-24-2	11.18
8	Triphenylmethanol (undecomposed)	68.05	260	76-84-6	68.66
9	9-Phenyl-9H-fluoren-9-ol	73.46	258	25603-67-2	0.58

TABLE 9.1.6. Examples of tertiary alcohols  $(R^1)(R^2)(R^3)C-OH$  that undergo fragmentation around  $450^\circ C$  with the formation a ketone  $R^1-CO-R^3$  and a hydrocarbon  $R^2H$  [22]

$R^1$	$R^2$	$R^3$
$CH_3-$	$n-C_4H_9-$	$n-C_4H_9-$
$CH_3-$	$C_6H_5CH_2-$	$CH_3-$
$CH_3-$	$CH_3-$	$C_6H_5-$
$CH_3-$	$CH_2=CHCH_3-$	$n-C_3H_7-$
$CH_3-$	$CH_3CH=CHCH_3-$	$n-C_4H_9-$
$CH_3-$	$CH_2=CHCH_3-$	$C_6H_5-$
$CH_3-$	$CH_3CH=CHCH_3-$	$C_6H_5-$
$CH_3-$	$CH_2=CHCH_3-$	$C_6H_5CH_2-$
$CH_3-$	$CH_3CH=CHCH_3-$	$C_6H_5CH_2-$
$CH_3-$	$(CH_3)_2CH-$	$(CH_3)_2C=CHCH_2CH_2-$
$CH_3-$	$n-C_4H_9-$	$CH_2=CHCH_2CH_2-$
$CH_3-$	$n-C_4H_9-$	$CH_3CH=CHCH_2CH_2-$
$CH_3-$	$C_6H_5CH_2-$	$CH_2=CHCH_2CH_2-$
$CH_3-$	$C_6H_5CH_2-$	$CH_3CH=CHCH_2CH_2-$
$CH_3-$	$CH_2=CHCH_2CH_2-$	$C_6H_5-$

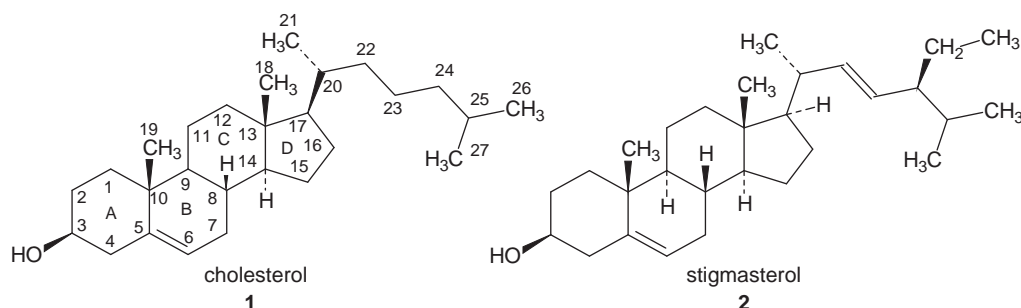
decomposition following a fragmentation reaction of the type 9.1.18 generating a ketone are listed in Table 9.1.6 [22]. As shown in Table 9.1.6, the lack of hydrogens on the carbon in the  $\beta$ -position to the OH group is not a requirement for molecule fragmentation. The increased temperatures of pyrolysis favor the fragmentation shown in reaction 9.1.5 with elimination of CO.

### Sterols

Sterols belong to a large class of natural compounds known as steroids. The steroids also include bile acids, sex hormones, cardiac aglycones and toad poisons, adrenal steroids, and steroidal sapogenins. Typical for sterols is the basic skeleton of perhydrocyclopentanophenanthrene with an OH group in 3-position, and it can be considered as deriving from the triterpene squalene. Sterols frequently are



classified based on their origin as plant sterols (phytosterols) or animal sterols (zoosterols). However, this classification is not strict, the zoosterol cholesterol, for example, being found also in red algae. Among phytosterols the more common ones are campesterol, sitosterol, and stigmasterol. From the zoosterols group, cholesterol is probably the best known. The structures of cholesterol and stigmasterol are shown below:



The OH group in sterols can be situated above the plane of the ring (indicated as  $\beta$ -positions) or below the plane of the ring (indicated as  $\alpha$ -position). Numerous other sterols are known in nature. Some compounds have completely saturated rings (which leads to an isomerism depending on the configuration of the A/B-ring junction, with a normal series for a *cis* A/B and an allo series for a *trans* A/B junction). Other sterols have more unsaturation in and outside the cycles (e.g. lumisterol and ergosterol). Numerous other compounds are related to sterols, including many steroids that contain a sterol structure with the OH group in the 3-position, but having additional functional groups. The nomenclature of sterols is described in the literature [23].

Sterols are typically stable to mild and moderate heating at temperatures up to 400 °C to 450 °C. The formation of an ether by elimination of water between two sterol molecules takes place when the compounds are heated around 250 °C for several hours. The conversion of stigmasterol as a function of increased temperature in a vacuum flash pyrolysis experiment is shown in Figure 9.1.8 [24]. Flash pyrolysis of cholesterol at 900 °C generates mainly cholest-4-en-3-one, cholest-3,5-diene, and cholesta-4,6-dien-3-one. Similarly, pyrolysis of stigmasterol generates stigmasta-4,22-dien-3-one, stigmastan-3,5,22-triene, etc. The main reactions of thermal decomposition for sterols proceed similarly to those of other secondary alcohols, including hydrogen and water eliminations, as indicated schematically below

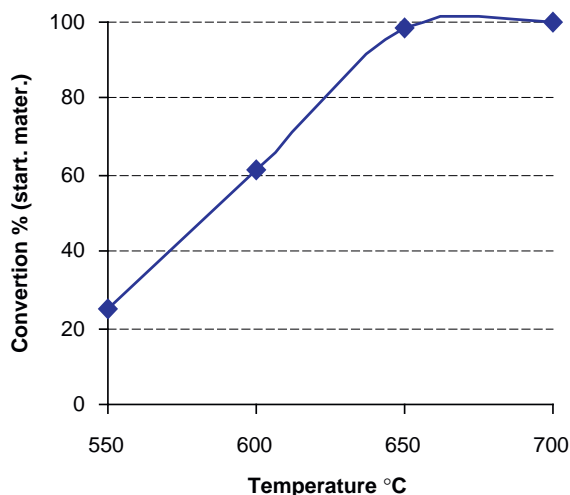
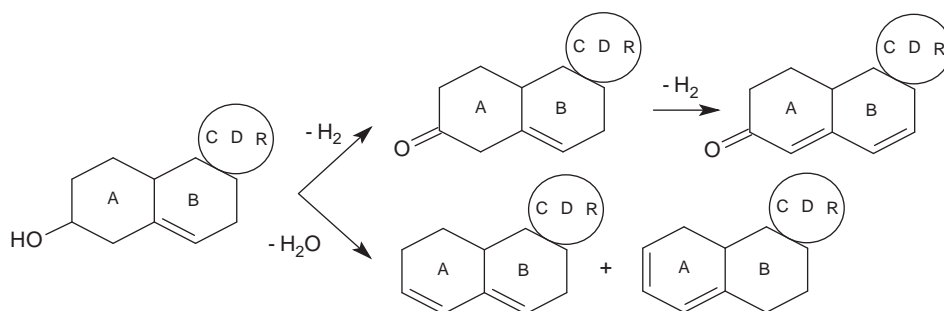


FIGURE 9.1.8. Conversion of stigmasterol in a flash vacuum pyrolysis experiment [24].

(R = various radicals attached to 17 position on cycle D):



Lower levels of other fragment molecules are generated, for example by the cleavage of the bond between C17 and C20 atoms. Also, the migrations of double bonds, preexistent or resulting from the H<sub>2</sub> or H<sub>2</sub>O elimination, can lead to unsaturation in other positions such as position C7 of the sterol molecule. Among the pyrolysis products identified are unsaturated aliphatic hydrocarbons such as hexatriene, various isomers of heptadiene, cyclic hydrocarbons such as methylcyclopentadiene, and fragments of the initial sterol [24].

At higher temperatures, sterols decompose by various fragmentation and dehydrogenation reactions to generate PAHs such as phenanthrene, anthracene, pyrene, chrysene, benz[a]anthracene, and their monomethylated derivatives. A study performed with either flash vacuum pyrolysis or atmospheric pressure flow pyrolysis (0.1–2.0 s heating time) at 700 °C on a series of structurally different plant steroids attempted to determine the influence of steroid structure on the formation of three-, four-, and five-ring PAHs [24]. The sterols studied included stigmaterol, stigmateryl acetate,  $\beta$ -sitosterol, stigmasta-3,5-diene, cholesterol, cholesteryl acetate, dihydrocholesterol, and ergosterol, with description of their structures given in Table 9.1.7.

Besides fragments of the initial sterol molecule, pyrolysis of sterols generates various aromatic compounds. The major aromatic compounds generated by flash vacuum pyrolysis at 700 °C of  $\beta$ -sitosterol, stigmasta-3,5-diene, cholesterol, cholesteryl acetate, and dihydrocholesterol are shown in Table 9.1.8 [24,25]. The experiment was performed in a quartz reaction tube packed with quartz chips with a heated zone of 30 cm and at  $10^{-4}$  Torr pressure. The rate of throughput of sample was 50–100 mg/h, and the calculated residence time in the heated zone of the parent compound was 0.190 s.

The sterols containing OH groups also show in their pyrolysates the presence of compounds retaining the OH group, such as 2-hydroxytetrahydronaphthalene, dimethyldecahydrophenanthren-2-ol, and other sterol fragment alcohols.

TABLE 9.1.7. Descriptions of the structure of several sterols with pyrolysis results reported in the literature [24]

Compound	Description of structure
Cholesterol	Cholest-5-en-3 $\beta$ -ol (formula 1 above)
Stigmaterol	Stigmasta-5,22-dien-3 $\beta$ -ol (formula 2 above)
Stigmateryl acetate	CH <sub>3</sub> COO attached on atom C3 of stigmaterol (formula 2 above)
$\beta$ -Sitosterol	Ethyl radical attached to C24 of cholesterol (formula 1 above)
Stigmasta-3,5-diene	No OH group on C3, double bond between C3 and C4, single bond between C22 and C23 on stigmaterol (formula 2 above)
Cholesteryl acetate	CH <sub>3</sub> COO attached to atom C3 on cholesterol (formula 1 above)
Dihydrocholesterol	Single bond between C5 and C6 on cholesterol (formula 1 above)
Ergosterol	Ergosta-5,7,22-trien-3 $\beta$ -ol, double bond C7–C8, methyl on C24 on stigmaterol (formula 2 above)

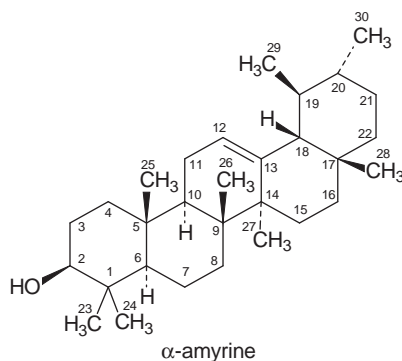
TABLE 9.1.8. *The major aromatic compounds identified in the pyrolysate of several sterols in mg/g sterol [24,25] at 700°C*

No.	Compound	$\beta$ -sitosterol	Stigmasta-3,5-diene	Cholesterol	Cholesteryl acetate	Dihydrocholesterol
1	Benzene	16.94	?	11.17	12.38	9.12
2	Toluene	18.89	?	23.61	20.05	19.18
3	Ethylbenzene	5.87	2.66	5.64	6.77	4.59
4	<i>m</i> + <i>p</i> -Xylene	3.87	1.53	4.05	3.07	3.42
5	Styrene	9.05	5.73	10.08	16.40	4.12
6	<i>o</i> + <i>p</i> -Ethyltoluene	3.66	2.41	4.87	4.09	4.32
7	$\alpha$ + $\beta$ -Methylstyrene	1.96	1.68	2.10	3.01	1.62
8	<i>o</i> + <i>p</i> -Methylstyrene	5.10	3.55	5.72	5.53	4.44
9	Indane	1.39	0.91	1.62	1.19	1.33
10	Indene	1.37	0.90	8.03	8.76	4.77
11	Methylindene+isomers	7.80	7.28	9.89	13.58	1.56
12	1,2-Dihydronaphthalene	4.28	7.05	3.83	7.50	1.66
13	Naphthalene	5.05	6.81	4.31	7.29	1.75
14	2-Methylnaphthalene	2.11	2.28	2.04	2.08	1.03
15	1-Methylnaphthalene	5.00	7.16	5.47	7.45	1.27
16	1-Ethylnaphthalene	5.68	4.73	3.28	4.88	1.05
17	Acenaphthylene	2.69	2.06	1.78	2.25	0.80
18	Acenaphthene	1.37	0.89	0.86	0.99	0.59
19	Fluorene	0.00	0.00	1.61	1.71	0.19
20	Phenanthrene	1.20	2.61	1.27	2.05	0.25
21	Anthracene	0.42	0.87	0.46	0.90	0.20
22	Methylphenanthrene+methylanthracene	2.93	2.79	2.34	3.31	0.49
23	Fluoranthene	0.00	0.00	0.14	0.11	0.00
24	Pyrene	0.22	0.42	0.22	0.29	0.00
25	Methylpyrenes	0.40	0.86	1.45	1.04	0.00
26	Benz[ <i>a</i> ]anthracene	0.27	0.14	0.00	0.00	0.00
27	Chrysene	0.26	0.17	0.38	0.17	0.00
28	Methylbenz[ <i>a</i> ]anthracene+methylbenz[ <i>a</i> ]chrysene	0.00	0.00	0.00	0.00	0.00
	Total	107.78	65.49	116.22	136.85	67.75

Since the steroids include a variety of compounds, other steroids may show specific fragments in their pyrolysates. For example, the aglycon in cardiac glycosides contains an additional OH group attached in 14-position of perhydrocyclopentanophenanthrene structure, and the R group is either an unsaturated butyrolactone (in cardenolides) or a  $\alpha$ -pyrone ring (in bufadienolides). These radicals are likely to generate furan and pyrone fragments in pyrolysates from these steroids.

The formation of PAHs is the result of a series of unimolecular reactions involving free radicals. PAH yields are most sensitive to the number of double bonds in the steroid B-ring. Ergosterol produced 13-fold more PAHs than dihydrocholesterol in flash vacuum pyrolysis and fourfold more PAHs in the flow pyrolysis experiments. Increasing the temperature from 700 °C to 800 °C in the flash vacuum pyrolysis experiments only slightly increased the PAH yields for dihydrocholesterol relative to cholesterol, but the yield of small aromatic hydrocarbons, such as benzene and toluene, increased approximately twofold. Small increases in PAH yields (10–40%) were found in the flash vacuum pyrolysis experiments if a double bond was placed in the steroid A-ring by 1,2-elimination of an ester (as for cholesteryl acetate), but this trend was not observed in the flow pyrolysis experiments. The PAH yields from the flow pyrolysis of steroids esterified with saturated and unsaturated long-chain fatty acids, i.e. cholesteryl stearate, cholesteryl oleate, and cholesteryl linolenate, were 20–40% lower (per gram of steroid) than the yields for the free steroids. The yield of three- to five-ring PAHs did not correlate with the number of double bonds in the ester chain, but the yield of benzene increased as the number of double bonds in the ester chain increased. The formation of PAHs from sterols has been reported also in connection with the formation of PAHs in cigarette smoke from the existing phytosterols from tobacco [18,26–30].

Terpene alcohols with smaller or larger molecules than sterols are common as natural products. As an example,  $\alpha$ - and  $\beta$ -amyrine are pentacyclic triterpenoids (derived from squalene) that contain an OH group. These compounds can be considered derivatives of picene (1,2:7,8-dibenzo-phenanthrene). Amyrines are very stable to pyrolysis. At temperatures higher than 700 °C, the amyrynes generate fragment molecules containing one or more cyclohexane cycles, some with partial unsaturation. Pyrolysis of these compounds at higher temperatures also generates aromatic molecules.



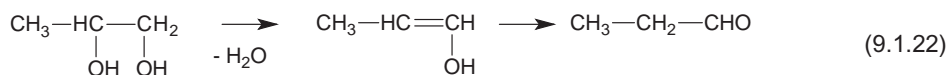
## Diols

Compounds with two OH groups in the molecule are diols. The two OH groups can be attached to adjacent carbon atoms (vicinal position) or to separate carbon atoms. The presence of two OH groups on the same carbon (geminal diols) also is possible, but it leads to unstable compounds. The simplest diol is ethylene glycol or 1,2-ethanediol ( $\text{HOCH}_2\text{—CH}_2\text{OH}$ ). The compound (b.p. 196–198 °C) begins decomposing around 500 °C. Formation of acetaldehyde and  $\text{H}_2\text{O}$  is a typical decomposition reaction for ethylene glycol, and it takes place as shown below:



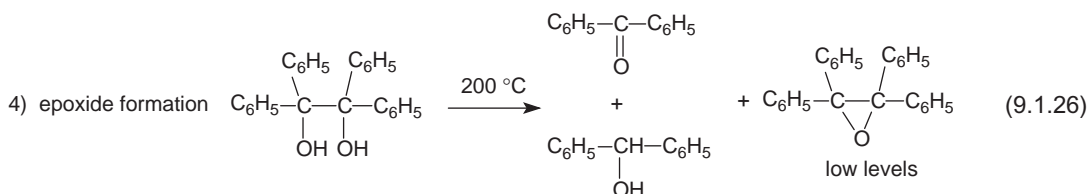
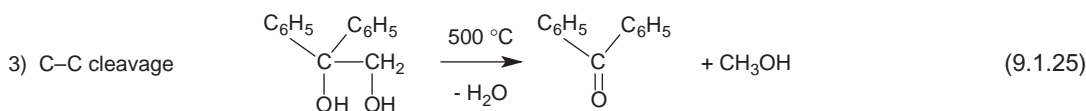
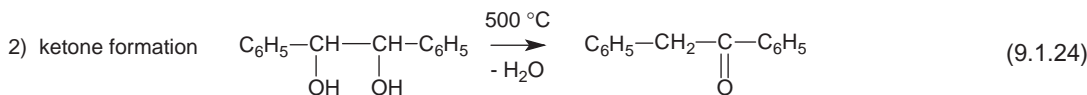
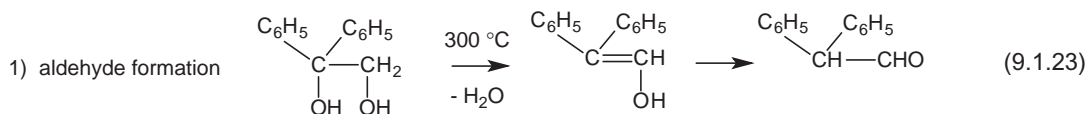
Besides acetaldehyde,  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$  also are generated during thermal decomposition of ethylene glycol. Traces of other compounds, such as crotonaldehyde ( $\text{CH}_3\text{—CH=CH—CHO}$ ), which may be formed from the condensation of two acetaldehyde molecules, are present at low levels in the pyrolysate. The methane and  $\text{CO}$  are possibly the result of further decomposition of acetaldehyde and not the result of an initial reaction from the diol.

Propylene glycol (PG) decomposes around  $500^\circ\text{C}$ , similarly to ethylene glycol, to form propionaldehyde.



It is interesting that acetone and hydroxyacetone are not major products of PG thermal decomposition. This indicates that the elimination of water takes place at the secondary alcohol group, and the hydrogen elimination expected for a secondary alcohol is not a likely reaction during PG pyrolysis. Also, the pyrolysis mechanism does not involve as an intermediate step the formation of propylene oxide (see Section 10.1.1), which would further generate both propionaldehyde and acetone.

Pyrolysis of other vicinal diols may lead to different types of reactions such as (1) reactions similar to 9.1.21 with the formation of an aldehyde, (2) reactions with water elimination but formation of a ketone (water elimination from the secondary alcohol group), (3) cleavage of a C—C bond with the formation of molecular fragments, and (4) elimination of water with the formation of an epoxide. The outcome of the reaction depends on the other substituents on the carbons bearing the OH groups and on the pyrolysis temperature. Some examples of these reaction types are given below:



The cleavage of a C—C bond in the alcohol molecule is typically favored by higher temperatures, while water elimination without fragmentation occurs typically at lower temperatures.

The diols with the OH groups in 1,3 positions frequently have each of the OH groups behaving similarly to those in monohydroxy alcohols. For example, thermal decomposition of 2-methylheptane-2,4-diol starts with  $\text{H}_2\text{O}$  elimination from the tertiary alcohol group to generate 2-methyl-2-heptene-4-ol and upon further decomposition to form 2-methyl-2,4-heptadiene and other octadienes. Propane-1,3-diol thermal decomposition proceeds in the same manner. The first step of decomposition is the

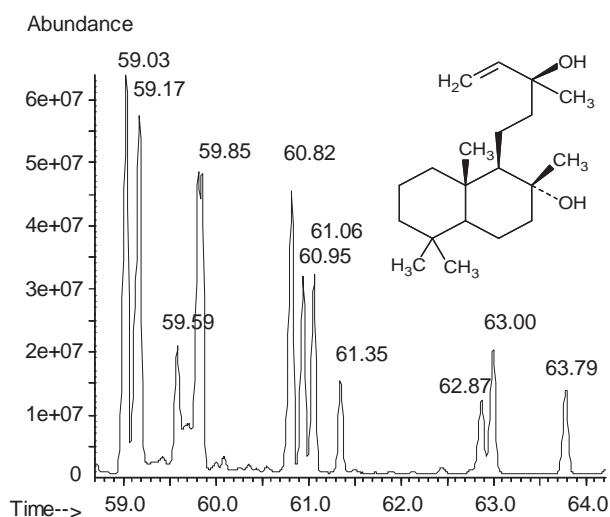


FIGURE 9.1.9. Time window 59–64 min from the pyrogram of sclareol at 900°C.

TABLE 9.1.9. Identification of the main peaks in the chromatogram shown in Figure 9.1.9 for the pyrolysis of sclareol at 900°C (some peak identifications were tentative only)

<p>R.T. = 59.03, MW = 272 ~16.30%</p>	<p>R.T. = 59.17, MW = 272 ~17.27%</p>	<p>R.T. = 59.59, MW = 272 ~5.89%</p>	<p>R.T. = 59.82, MW = 272 ~10.57%</p>
<p>R.T. = 59.85, MW = 272 ~8.44%</p>	<p>R.T. = 60.82, MW = 272 ~11.72%</p>	<p>R.T. = 60.95, MW = 290 ~6.96%</p>	<p>R.T. = 61.06, MW = 290 ~6.90%</p>
<p>R.T. = 61.35, MW = 290 ~3.45%</p>	<p>R.T. = 62.87, MW = 290 ~3.38%</p>	<p>R.T. = 63.00, MW = 308 ~4.88%</p>	<p>R.T. = 63.79, MW = 306 ~3.34%</p>

formation of allyl alcohol. Further elimination of  $H_2$  leads to the formation of acrolein. Part of the  $H_2$  eliminated in this reaction can hydrogenate some of the allyl alcohol to 1-propanol. Pyrolysis of other diols with practical or potential applications and of common diols but performed under special pyrolysis conditions such as catalysts or critical water are reported in the literature [31–33].

Many more complex molecules have two OH groups in their structure. When these OH groups are isolated and the molecule is complex, the pyrolysis outcome is determined both by typical simple alcohol reactions and by the molecular overall structure. For example, sclareol is a diol derived from a labdane type diterpene (1*R*,2*R*,8*aS*)-decahydro-1-(3-hydroxy-3-methyl-4-pentenyl)-2,5,5,8*a*-tetramethyl-1-naphthol. A pyrolysis of 1 mg sclareol was performed using Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900^\circ C$ ,  $\beta = 10^\circ C/ms$ , THT = 10 s, and housing temperature  $T_{hou} = 280^\circ C$ . The time window between 59 min and 64 min from the resulting pyrogram, which contains the main decomposition products, is shown in Figure 9.1.9.

The analysis of the pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications in the pyrogram window and their relative molar content in 100 moles of pyrolysate are given in Table 9.1.9. The calculation of the mole % was obtained based solely on peak areas. In addition to the major peaks identified in the pyrogram and shown in Figure 9.1.9, several other compounds at lower levels were present. Among these were identified 1,7,7-trimethyl-2,3-dimethylenebicyclo[4.4.0]-decane (MW = 204) and 1,7,7-trimethyl-2-vinylbicyclo[4.4.0]dec-3-ene (MW = 204).

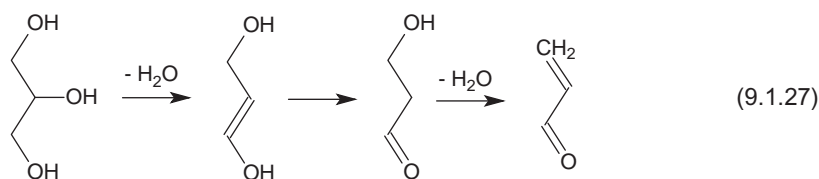
About 4.9% sclareol (eluting at 63.00 min) remained undecomposed during pyrolysis in the selected pyrolysis conditions.

### Glycerin

Glycerin (glycerol or propane-1,2,3-triol) is a compound widespread in nature either in free form or, more frequently, as esters (glycerides). Glycerin can be considered a sugar alcohol formed by hydrogenation from glycerin aldehyde (a  $C_3$  monosaccharide). Large quantities of glycerin are synthesized from epichlorhydrin and are generated as a by-product in soap making and biodiesel production. Glycerin is used as a humectant in food, beverages and tobacco industries, as a solvent and sweetener, and as a thickening agent.

At temperatures below  $350^\circ C$ , particularly in the presence of silica, metals, and certain salts such as  $MgSO_4$  and  $K_2HPO_4$ , glycerin forms small amounts of acrolein. Formation of acrolein from the pyrolysis of glycerin is of particular concern, since glycerin is added as a humectant on cigarettes [34]. At temperatures around  $450^\circ C$ , acetaldehyde and allyl alcohol are formed also. At even higher temperatures ( $650^\circ C$ ) glycerin vapors in the presence of water vapors show even at short residence time (0.1 s) about 15% decomposition, with the formation of acrolein, acetaldehyde, and formaldehyde as the main reaction products (in addition to water). The decomposition percent increases considerably at  $750^\circ C$ , where the glycerin decomposition is almost complete. At this temperature other compounds also are present in the pyrolysate as a result of subsequent decomposition of acrolein and acetaldehyde as well as of different paths of direct glycerin decomposition [35,36]. Among the secondary pyrolysis products are  $CO$ ,  $H_2$ ,  $CH_4$ , and  $C_2H_4$ . Traces of  $CO_2$ ,  $C_2H_6$ ,  $C_3H_6$ , 1,3-butadiene, and isobutene also were detected in the pyrolysate. Figure 9.1.10 shows the variation of pyrolysis products of glycerin (diluted to about 1% with steam) in moles per 100 moles converted glycerin at different temperatures. The residence times in the pyrolyzer were 0.13 s for  $650^\circ C$  and  $675^\circ C$  and 0.048 s for  $700^\circ C$  [35].

The pyrolysis mechanism of glycerin pyrolysis very likely consists of both radical initiated reactions and nonradical initiated reactions. The formation of acrolein would be expected to occur as the result of the following sequence:



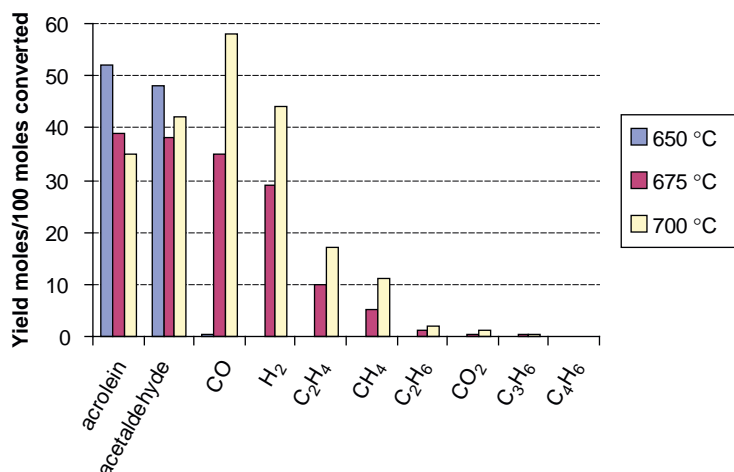
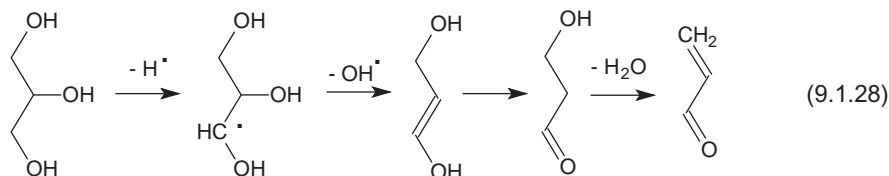


FIGURE 9.1.10. Variation of pyrolysis products of glycerin (diluted with steam) in moles per 100 moles converted glycerin at different temperatures and a residence time of 0.13 s for 650 and 675 °C and of 0.048 s for 700 °C [35].

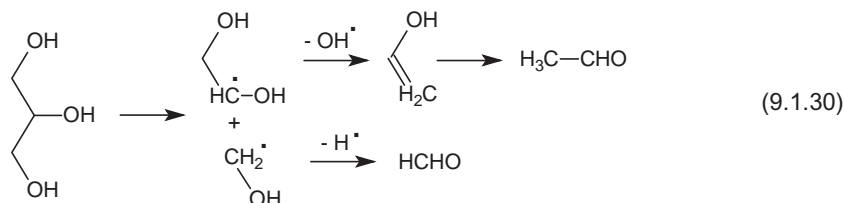
However, free radical inhibitors such as NO affect the formation of acrolein. For this reason, a mechanism involving free radicals is considered as dominant in the acrolein formation, shown as follows:



The decomposition following reaction 9.1.28 to the step of an aldol formation can continue with a retro-aldol reaction, as shown below [36]:



Acetaldehyde also can be generated directly from glycerin by radical reactions as shown below:



However, both reactions 9.1.29 and 9.1.30 predict the formation of equal quantities of formaldehyde and acetaldehyde, which is not in agreement with the experimental data. Possibly some formaldehyde is decomposed into H<sub>2</sub> and CO, or other fragments are generated as a side result of reaction 9.1.28.

The study of the kinetics of glycerin decomposition [35] indicated that the reaction can be considered unimolecular and follows the Arrhenius equation:

$$k = (1.52 \pm 0.15) 10^{+13} \exp \left[ \frac{-(55.6 \pm 5.5) 10^{+3}}{RT} \right] \text{s}^{-1} \quad (9.1.31)$$



One potential application of glycerin pyrolysis is the production of combustible gas mixtures. Since glycerin is a by-product of several industrial processes particularly related to biodiesel, an excess of glycerin would be available on the market if biodiesel production increased. For this reason, glycerin utilization for generation of gaseous fuels such as  $H_2$ , of synthesis gas (syn gas), or of  $CH_3OH$  is of considerable interest. Since pyrolysis of glycerin at elevated temperatures (around 800 °C) produces mainly a mixture of  $CO$ ,  $H_2$ ,  $CO_2$ ,  $CH_4$ , and  $C_2H_4$  (similar to that of synthesis gas), various studies were geared toward the optimization of this process [37,38].

## Polyols

The polyols are compounds with more than two or three OH groups on an aliphatic chain. Some of the more common polyols are sugar alcohols. They can be obtained by the hydrogenation of a carbohydrate and have a name derived from the carbohydrate from which they were generated. Among those sugar alcohols are erythritol ( $C_4H_{10}O_4$ ), arabitol ( $C_5H_{12}O_5$ ), xylitol ( $C_5H_{12}O_5$ ), ribitol ( $C_5H_{12}O_5$ ), glucitol (sorbitol) ( $C_6H_{14}O_6$ ), 1,5-anhydrosorbitol (styracitol) ( $C_6H_{12}O_5$ ), mannitol ( $C_6H_{14}O_6$ ), and primulitol ( $C_7H_{16}O_7$ ). Sugar alcohols are frequently found in nature in fruits and vegetables. Some sugar alcohols are used as food additives due to their relatively sweet taste and low caloric contribution. Also, some are used as humectants. Mannitol is used as a diuretic. Sugar alcohols contain asymmetric carbons in their molecule and some are stereoisomers of each other. For example, glucitol is (2*R*,3*S*,4*S*,5*S*)-hexane-1,2,3,4,5,6-hexol, while mannitol is (2*R*,3*R*,4*R*,5*R*)-hexane-1,2,3,4,5,6-hexol. Other polyols include inositol (the common naturally occurring form being *myo*-inositol or *cis*-1,2,3,5-*trans*-4,6-cyclohex-anhexol), as well as partially hydrogenated disaccharides such as lactitol ( $C_{12}H_{24}O_{11}$ ) and maltitol ( $C_{12}H_{24}O_{11}$ ). Maltitol (4-*O*- $\alpha$ -D-glucopyranosyl-D-glucitol), for example, is obtained by partial hydrogenation of the disaccharide maltose. It contains a glucitol residue and a glucopyranosyl residue, making this substance half alcohol and half carbohydrate.

Mild heating of sugar alcohols does not lead to a browning process as happens when sugars are heated. Their stability to thermal decomposition is higher than that of saccharides. A pyrogram of a glucitol sample is given in Figure 9.1.11. The experiment was performed on 1.0 mg compound using Type 2a Experiment as described in Section 4.6, at  $T_{eq} = 900$  °C,  $\beta = 10$  °C/ms, THT = 10 s, and housing temperature  $T_{hou} = 280$  °C. The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications in the pyrogram and their relative molar content in 100 moles of pyrolysate are given in Table 9.1.10. The calculation of the mole % was obtained based solely on peak areas.

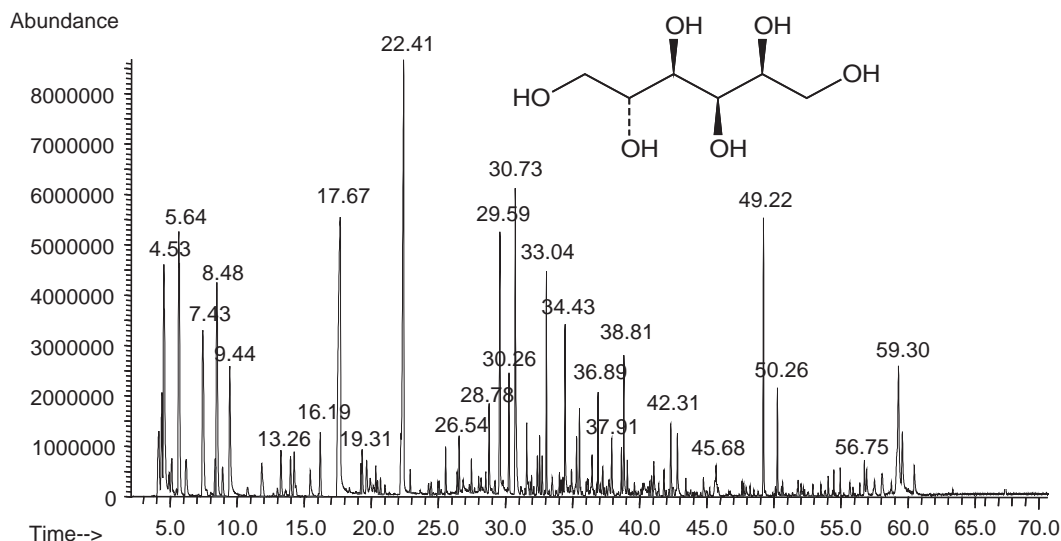


FIGURE 9.1.11. Pyrogram of glucitol ( $C_6H_{14}O_6$ ) at 900 °C. Peak assignment is given in Table 9.1.10.

TABLE 9.1.10. Identification of the main peaks in the chromatogram shown in Figure 9.1.11 for the pyrolysis of glucitol (hydrogen, methane, ethylene, and water were not analyzed due to the mass spectrometer settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Propene	4.39	42	115-07-1	3.03
2	Formaldehyde	4.53	30	50-00-0	12.88
3	1-Butene	4.93	56	106-98-9	0.59
4	1-Butyne	5.12	54	107-00-6	1.04
5	Acetaldehyde	5.64	44	75-07-0	9.32
6	Methanol	6.19	32	67-56-1	2.02
7	Furan	7.43	68	110-00-9	4.16
8	1,3-Cyclopentadiene	8.36	66	542-92-7	0.67
9	2-Propenal	8.48	56	107-02-8	5.71
10	Acetone	8.91	58	67-64-1	0.68
11	2-Butanone	9.44	72	78-93-3	2.84
12	2,3-Dihydrofuran	10.78	70	1191-99-7	0.34
13	2-Methylfuran	11.83	82	534-22-5	0.68
14	2-Propen-1-ol	13.26	58	107-18-6	0.93
15	Butenal	13.57	72	123-72-8	0.33
16	Methyl vinyl ketone	13.97	70	78-94-4	0.64
17	2,3-Butanedione	14.24	86	431-03-8	0.48
18	1-Methyl-1,3-cyclopentadiene	15.44	80	96-39-9	0.48
19	Benzene	16.19	78	71-43-2	0.90
20	Hydroxyacetaldehyde	17.67	60	141-46-8	12.11
21	2-Butenal (Z)	19.22	70	15798-64-8	0.34
22	2-Butenal (E)	19.31	70	123-73-9	0.63
23	1,2-Propandiol	19.65	76	4254-15-3	0.53
24	Acetic acid	19.91	60	64-19-7	0.44
25	1,4-Pentadien-3-one	20.33	82	1890-28-4	0.29
26	4-Pentenal	20.46	84	2100-17-6	0.13
27	Vinylfuran	20.69	94	1487-18-9	0.15
28	Ethyl-1-propenyl ether?	22.21	86	928-55-2	0.38
29	1-Hydroxy-2-propanone	22.41	74	116-09-6	9.44
30	Toluene	22.90	92	108-88-3	0.17
31	3-Penten-2-one	24.27	84	3102-33-8	0.12
32	3-Hydroxy-2-butanone	24.46	88	513-86-0	0.15
33	2,3-Dihydro-1,4-dioxin	24.97	86	543-75-9	0.10
34	Propanoic acid	25.06	74	79-09-4	0.14
35	2-Pentenal (E)	25.21	84	1576-87-0	0.03
36	3-Methylfuran	25.55	82	930-27-8	0.41
37	2H,4H-1,3-Dioxin	26.40	86	N/A	0.19
38	2,2'-Bioxirane?	26.55	86	298-18-0	0.51
39	1-Hydroxy-2-butanone	27.46	88	5077-67-8	0.27
40	2(5H)-Furanone	28.78	84	497-23-4	0.88
41	2-Oxopropionic acid methyl ester?	29.22	102	600-22-6	0.13
42	Butandial	29.59	86	638-37-9	3.04
43	Styrene	29.81	104	100-42-5	0.14

(Continued)

TABLE 9.1.10. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
44	Furfural	30.26	96	98-01-1	0.47
45	2-Cyclopentenone	30.28	82	930-30-3	0.30
46	2-Propylfuran	30.73	110	4229-91-8	2.92
47	2-Furanmethanol	31.58	98	98-00-0	0.65
48	5-Methyl-2(3H)-furanone	31.94	98	591-12-8	0.14
49	2-Methoxyfuran	32.72	98	25414-22-6	0.06
50	1-(2-Furanyl)ethanone	33.04	110	1192-62-7	1.31
51	Cyclopropyl ketone?	33.49	110	1121-37-5	0.19
52	Dihydro-4-hydroxy-2(3H)-furanone	34.02	102	5469-16-9	0.17
53	Dihydro-3-methylene-2(3H)-furanone	34.28	98	547-65-9	0.13
54	2-Hydroxy-2-cyclopenten-1-one	34.43	98	10493-98-8	1.55
55	Unknown	34.92	110	N/A	0.23
56	2-Cyclohexen-1-ol	35.30	98	822-67-3	0.56
57	5-Methyl-2-furancarboxaldehyde	35.51	110	620-02-0	0.58
58	Mixture	36.45	112	N/A	0.40
59	3-Propylfuran	36.89	110	N/A	0.67
60	Unknown	37.24	128	N/A	0.24
61	2-Hydroxy-3-methyl-2-cyclopenten-1-one	37.91	112	80-71-7	0.46
62	Phenol	38.63	94	108-95-2	0.35
63	1,5-Hexadien-3-ol	38.82	98	924-41-4	1.21
64	2-Cyclohexen-1,4-dione	39.07	110	4505-38-8	0.23
65	2-(2-Furanmethyl)-5-methyl-furan	40.23	162	13678-51-8	0.06
66	Glycerin	40.32	92	56-81-5	0.33
67	4-Heptyn-3-ol	40.74	112	32398-69-9	0.11
68	3-Furancarboxylic acid methyl ester	40.89	126	13129-23-2	0.20
69	2,2-Dimethyl-1-pentanol	41.05	116	2370-12-9	0.38
70	3-Methyl-2-cyclohexen-1-one	41.41	110	1193-18-6	0.11
71	Cyclopenten-3,4,5-triol	41.80	116	29782-84-1	0.18
72	5-(Hydroxymethyl)dihydro-2(3H)-furanone	42.31	116	32780-06-6	0.60
73	1-(2-Furanyl)-1,2-ethanediol	42.81	128	19377-75-4	0.53
74	Unknown	43.43	112	N/A	0.10
75	Unknown	44.75	128	N/A	0.15
76	Cyclopentane-1,2-diol	45.68	102	N/A	0.42
77	Catechol (1,2-benzenediol)	47.75	110	120-80-9	0.08
78	1,4:3,6-Dianhydro-D-glucitol (isosorbide)	49.22	146	652-67-5	1.41
79	6,8-Dioxabicyclo[3.2.1]octane-diol	50.26	146	N/A	0.51
80	Hydroquinone	50.65	110	123-31-9	0.10
81	Dianhydrosugar	51.81	146	N/A	0.12
82	Anhydro-D-galactosan	52.02	144	N/A	0.05
83	Unknown	53.51	176	N/A	0.05
84	Anhydrosugar	54.47	164	N/A	0.11
85	Dianhydrosugar	55.65	146	N/A	0.11
86	Unknown	56.41	156	N/A	0.05

(Continued)

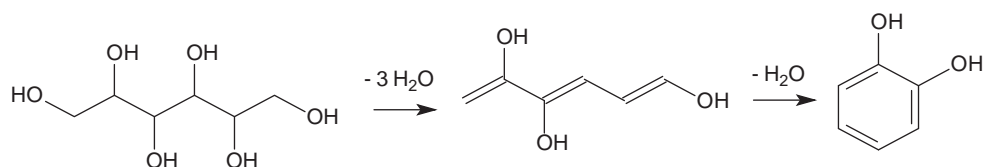
TABLE 9.1.10. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
87	1,6-Anhydro- $\beta$ -D-glucopyranose (levoglucosan)	56.75	162	498-07-7	0.18
88	Anhydrosugar	56.91	164	N/A	0.17
89	1,4-Anhydromannitol	57.43	164	7726-97-8	0.16
90	Anhydrosugar	58.06	164	N/A	0.25
91	1,4-Anhydro-D-glucitol	59.30	164	27299-12-3	1.50
92	1,5-Anhydroglucitol	59.57	164	154-58-5	0.49
93	Polygalitol	60.47	164	N/A	0.22

As shown in Figure 9.1.11 and Table 9.1.10, the composition of glucitol pyrolysate is rather complex. However, the list of components is still incomplete, some very polar compounds, including not decomposed parent glucitol, not being seen in the pyrogram from Figure 9.1.11. This incompleteness occurs because polar nonvolatile compounds do not elute from the chromatographic column in the selected conditions. The extension of information on highly polar compounds is achieved with an offline pyrolysis that was performed on 1.0 mg glucitol and conditions described by Type 2b Experiment from Section 4.6. The pyrolysis conditions were  $T_{eq} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280^\circ\text{C}$ . The pyrolysate was derivatized with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) in dimethylformamide (DMF) (2:1, v:v) and analyzed by GC/MS in conditions as described in Table 4.6.2. A number of compounds already listed in Table 9.1.10, which have OH groups and can be derivatized to trimethylsilyl ethers (TMS derivative), were detected in the pyrolysate. In addition to those compounds, parent glucitol, as well as low levels of other hexitols, glucose, fructose, and other monosaccharides were found in the pyrolysate. The monosaccharides were generated by a dehydrogenation reaction from glucitol.

Results from previous experiments show that pyrolysis of glucitol occurs by typical reactions for alcohols. These include water elimination with or without molecular fragmentation, hydrogen elimination, and formation of internal ethers. Also, Grob fragmentation (with the formation of aldehydes) and pinacol rearrangements with retro-aldol fragmentation can occur. These types of reactions account for formation of a large number of aldehydes and ketones in pyrolysis of polyols. Common for larger molecules, numerous fragmentations also occur, as either initial or subsequent reactions.

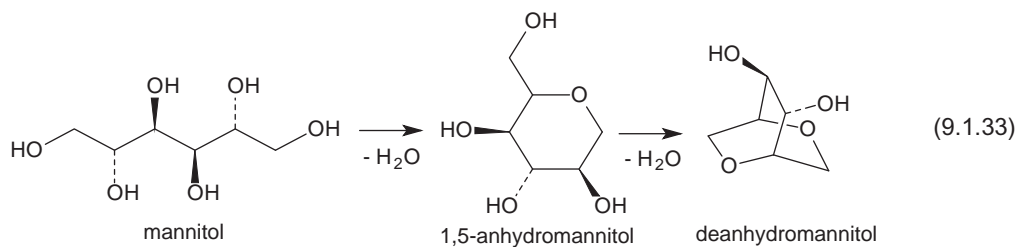
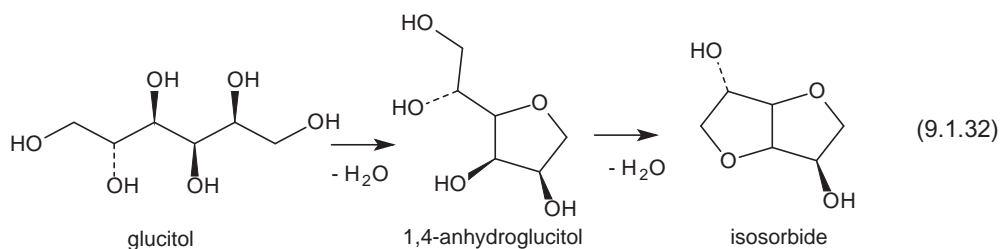
Some aromatic compounds including benzene, toluene, phenol, catechol, and hydroquinone also occur in the pyrolysate. Water elimination can be responsible for the formation of molecules such as catechol in a reaction as shown below:



However, it is likely that more complex sequences of reactions contribute to the formation of all aromatic compounds.

Mannitol generates by pyrolysis small fragments identical to those of glucitol. Even the relative molar content for most fragment molecules in the pyrolysate of mannitol is similar to that of glucitol. However, starting with the pyrolysis products where the differences in stereochemistry can be noticed, sorbitol and mannitol fragment molecules show differences. For example, by elimination of two water molecules, glucitol generates 1,4:3,6-dianhydro-D-glucitol (isosorbide) (Ret. time 49.22 min), while

mannitol generates dianhydromannitol (Ret. time 45.72 min). The two different reactions are shown below:



Reactions 9.1.32 and 9.1.33 show that the steric structure of the molecule influences the elimination of water. Also, when chiral atoms remain in the molecular fragment, they tend to preserve the steric arrangement from the parent molecule. Contrary to the high similarity in nature and quantity of the small molecular fragments of the two hexitols, considerable differences are seen for fragments retaining steric differences. This can be shown in a time window of 56–61 min in the pyrograms, where large anhydro sugar/anhydro sugar alcohol molecules elute. The comparison of the pyrogram window for glucitol (Figure 9.1.12A) with that for mannitol (Figure 9.1.12B) shows significant quantitative differences, although some of the compounds in the two pyrograms belong to the same anhydro sugars.

In Figure 9.1.12A the major peak at 59.30 min belongs to 1,4-anhydroglucitol and that at 59.57 to 1,5-anhydroglucitol, while for Figure 9.1.12B the peak at 57.45 min belongs to 1,4-anhydromannitol and that at 59.95 min belongs to 1,5-anhydromannitol.

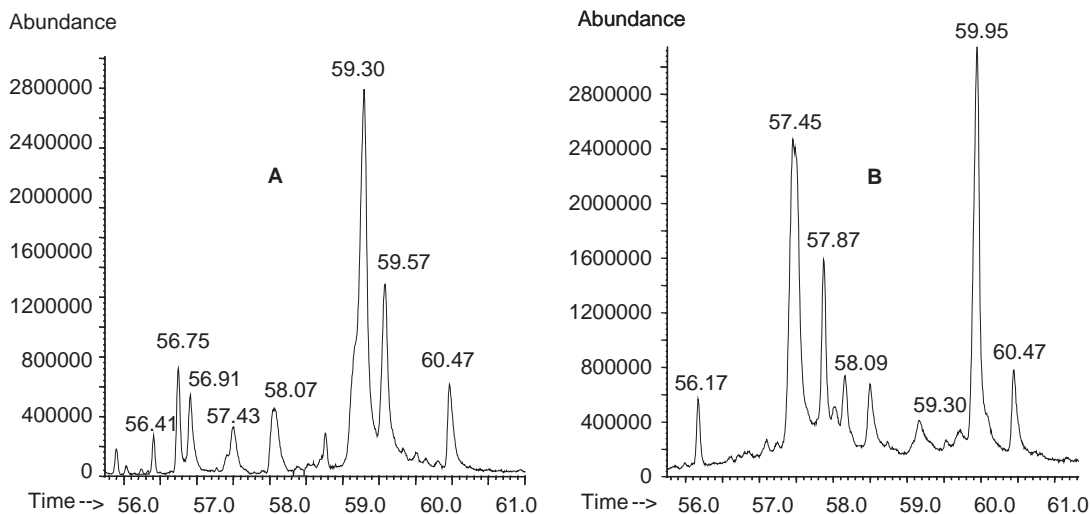


FIGURE 9.1.12. Time window of 56–61 min from a pyrogram of glucitol (Figure 9.1.12A) from a pyrogram of mannitol (Figure 9.1.12B).

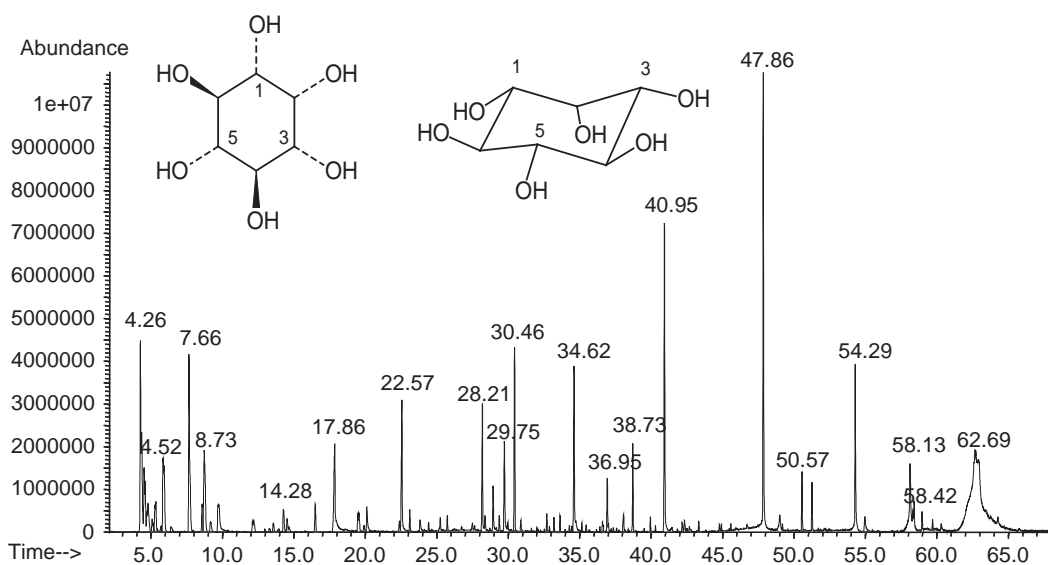
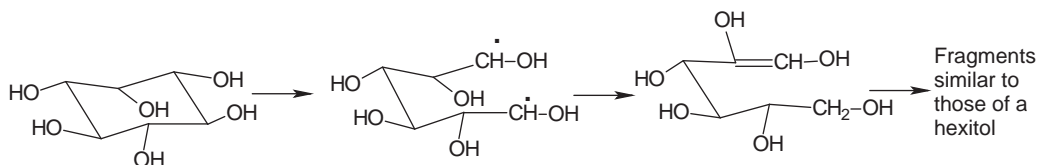


FIGURE 9.1.13. Pyrogram of *myo*-inositol ( $C_6H_{12}O_6$ ) at  $900^\circ C$ . Peak assignment is given in Table 9.1.11.

Small fragment molecules similar to those from glucitol and mannitol are generated in pyrolysis of other sugar alcohols. Also, similar small fragment molecules are obtained from compounds such as maltitol, which is only partly alcohol. Pyrolysis of maltitol will be discussed in Section 16.3.

As previously discussed in Chapter 2, the pyrolysis results for a molecule are influenced by both particular functional groups and by the overall structure of the molecule. As an example, inositol has functional groups similar to those of glucitol, for example, but the structures of the two molecules are different, one being a linear molecule with two primary alcohol groups and the second being a cyclic molecule with all OH groups on secondary carbons. Also, the steric positions of the OH groups in two molecules are different. A pyrogram of a *myo*-inositol ( $C_6H_{12}O_6$ ) sample is given in Figure 9.1.13. The experiment was performed on 1.2 mg compound using Type 2a Experiment as described in Section 4.6, at  $T_{eq} = 900^\circ C$ ,  $\beta = 10^\circ C/ms$ , THT = 10 s, and housing temperature  $T_{hou} = 280^\circ C$ . The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications in the pyrogram and their relative molar content in 100 moles of pyrolysate are given in Table 9.1.11. The calculation of the mole % was obtained based solely on peak areas.

As shown in Table 9.1.11, qualitatively the pyrolysis products of inositol are very similar to that of glucitol. The result is not surprising since under the influence of heat the cyclohexane ring is likely to be transformed into a linear molecule. As shown in Section 7.2 for cyclohexane, the six-carbon ring undergoes isomerization to 1-hexene (reaction 7.2.1) when pyrolyzed. The peak intensities for at least the first half of the pyrogram for inositol also are proportional to that for glucitol. In conclusion, one of the main reactions in inositol thermal decomposition is of the type:



The formation of numerous furan and of some pyran derivatives clearly indicates that the cyclohexane ring is opened during pyrolysis and is followed by some cyclization with the inclusion of the oxygen atoms in the ring.

TABLE 9.1.11. *Identification of the main peaks in the chromatogram shown in Figure 9.1.13 for the pyrolysis of myoinositol (hydrogen, methane, ethylene, water were not analyzed due to the mass spectrometer settings)*

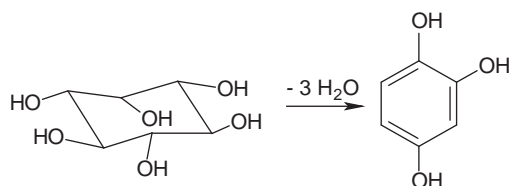
No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Carbon dioxide	4.26	44	124-38-9	11.73
2*	Propene	4.52	42	115-07-1	4.19
3*	Formaldehyde	4.79	30	50-00-0	4.02
4*	1-Butene	5.08	56	106-98-9	0.61
5*	1-Butyne	5.34	54	107-00-6	1.84
6*	Acetaldehyde	5.85	44	75-07-0	6.55
7*	Furan	7.66	68	110-00-9	6.10
8*	1,3-Cyclopentadiene	8.58	66	542-92-7	1.27
9*	2-Propenal	8.73	56	107-02-8	4.87
10*	Acetone	9.17	58	67-64-1	0.57
11*	2-Butanone	9.75	72	78-93-3	1.78
12*	2-Methylfuran	12.11	82	534-22-5	0.22
13	2-Methyl-2-propenal	12.19	70	78-85-3	0.49
14*	2-Propen-1-ol	13.57	58	107-18-6	0.39
15*	Methyl vinyl ketone	14.28	70	78-94-4	0.83
16*	2,3-Butanedione	14.54	86	431-03-8	0.28
17*	Benzene	16.51	78	71-43-2	0.73
18*	Hydroxyacetaldehyde	17.86	60	141-46-8	4.82
19*	2-Butenal (Z)	19.48	70	15798-64-8	0.42
20*	2-Butenal (E)	19.57	70	123-73-9	0.54
21*	Acetic acid	20.12	60	64-19-7	0.96
22*	Ethyl-1-propenyl ether?	22.40	86	928-55-2	0.22
23*	1-Hydroxy-2-propanone	22.57	74	116-09-6	3.51
24*	Toluene	23.13	92	108-88-3	0.31
25	Methyl formate	23.85	60	107-31-3	0.45
26*	Propanoic acid	25.26	74	79-09-4	0.31
27*	3-Methylfuran	25.75	82	930-27-8	0.26
28	2-Methyl-2-butenal	28.21	84	497-03-0	2.46
29	Cyclopentanone	28.39	84	120-92-3	0.31
30*	2(5H)-Furanone	28.96	84	497-23-4	0.83
31*	2-Oxopropionic acid methyl ester?	29.39	102	600-22-6	0.20
32*	Butandial	29.75	86	638-37-9	1.86
33*	1,2-Furancarboxaldehyde (furfural)	30.26	96	98-01-1	2.00
34*	2-Cyclopentenone	30.46	82	930-30-3	1.72
35*	2-Propylfuran	30.89	110	4229-91-8	0.18
36	Unknown	32.71	96	N/A	0.26
37*	1-(2-Furanyl)ethanone	33.22	110	1192-62-7	0.17
38	2-Cyclopentene-1,4-dione	33.64	96	930-60-9	0.22
39*	2-Hydroxy-2-cyclopenten-1-one	34.62	98	10493-98-8	3.13
40	Benzaldehyde	35.16	106	100-52-7	0.16
41	Butyrolactone	36.61	86	96-48-0	0.24
42	2-Methyl-2-butenal?	36.95	84	1115-11-3	1.09
43	2H-Pyran-2-one?	38.09	96	504-31-4	0.36
44*	Phenol	38.73	94	108-95-2	1.28

TABLE 9.1.11. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
45	Resorcinol	39.96	110	108-46-3	0.18
46*	3-Furancarboxylic acid methyl ester	40.95	126	13129-23-2	4.02
47	4-Methyl-5H-furan-2-one	42.18	98	6124-79-4	0.17
48	5-Hydroxymethyldihydrofuran-2-one	42.35	116	N/A	0.20
49	2,5-Furandicarboxaldehyde	43.35	124	823-82-5	0.11
50*	Catechol (1,2-benzenediol)	47.86	110	120-80-9	6.91
51	5-(1-Methylethyl)-2(5H)-furanone	49.02	126	56767-19-2	0.36
52*	Hydroquinone	50.57	110	123-31-9	0.75
53	Unknown	51.27	110	N/A	0.61
54	1,2,3-Benzenetriol (pyrogallol)	54.30	126	87-66-1	2.22
55	Unknown	54.97	144	N/A	0.32
56	1,2,4-Benzenetriol	58.13	126	533-73-3	1.89
57	1,3,5-Benzenetriol	58.32	126	108-73-6	0.32
58	Unknown	58.42	126	N/A	0.47
59	Dianhydrosugar	58.97	144	N/A	0.20
60	Maltol	59.71	126	118-71-8	0.10
61	Inositol	62.69	180	87-89-8	6.47

\*Compounds also identified in the pyrolysate of glucitol.

The differences in the pyrograms of inositol and a hexitol are obvious regarding hydroxybenzenes. Starting with phenol and continuing with dihydroxybenzenes, these compounds are at considerably higher levels in inositol pyrolysate. Trihydroxybenzenes are absent for glucitol pyrolysate and present for inositol pyrolysate. This finding indicates that water elimination from the cyclic molecule with the formation of double bonds followed by aromatization of the six-carbon cycle is another important process that takes place during inositol pyrolysis. Formation of 1,2,4-trihydroxybenzene is shown below:



For the formation of dihydroxybenzene (with a C/O ratio 3/1) and of phenol (with a C/O ratio 6/1), some mechanism for oxygen subtraction from the parent molecule (with a C/O ratio 1/1) should be present. Water elimination alone cannot account for the formation of phenol and of dihydroxybenzenes since there is not enough hydrogen in inositol to form an aromatic compound and eliminate more than three  $\text{H}_2\text{O}$  molecules. The formation of  $\text{CO}_2$  is probably involved in the elimination of part of the oxygen from the inositol molecule. Formation of char and  $\text{H}_2\text{O}$  (up to six molecules) also eliminates some of the oxygen.

Some aromatization with the formation of benzene rings also takes place starting with the linear chain of hexitols, but large differences in the yield of aromatic compounds are present between the pyrolysates of inositol and aliphatic hexitols.

### Metal alcóxides

The compounds known as alcóxides (or alcoholates) can be considered as formed from the conjugate base of an alcohol  $\text{RO}^-$  and a metal ion. Alcóxides of short-chain alcohols with monovalent metals such as sodium or potassium can be obtained directly from the reaction of the metal with the alcohol. Besides



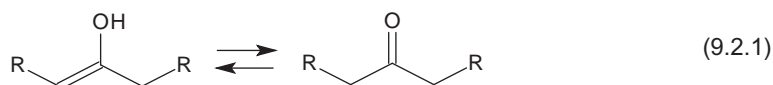
the alkoxides of monovalent metals ( $\text{Na}^+$ ,  $\text{K}^+$ , etc.), the alkoxides of other metals also are known, and, for example, the alkoxides of transitional metals are used for the manufacturing of special coatings and as catalysts. The formula of alkoxides of monovalent metals is  $\text{ROME}$ , for divalent metals  $(\text{RO})_2\text{Me}$ , etc.

As a rule, thermal decomposition of alkoxides takes place at considerably lower temperatures than those of the corresponding alcohol. For example, sodium methoxide decomposes around  $230^\circ\text{C}$  to form  $\text{H}_2$ , carbon,  $\text{Na}_2\text{CO}_3$ , and  $\text{Na}_2\text{C}_2$ . Thermal decomposition of  $(\text{CH}_3\text{O})_2\text{Ba}$  around  $350^\circ\text{C}$  leads to the formation of  $\text{H}_2$ ,  $\text{BaO}$ ,  $\text{BaCO}_3$ , and carbon. At about  $300^\circ\text{C}$ ,  $\text{C}_2\text{H}_5\text{ONa}$  decomposes with the formation of  $\text{NaOH}$  and  $\text{C}_2\text{H}_4$  [22]. The formation of the corresponding olefin was noticed in the thermal decomposition of other sodium alkoxides. The lower stability of alkoxide compared to that of the corresponding alcohol is true also for glycerin.

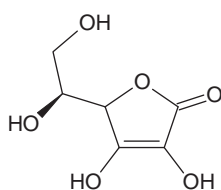
## 9.2. ENOLS

### General aspects

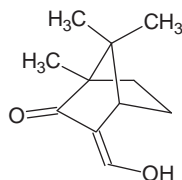
Enols are compounds containing the OH group bound to a carbon involved in a double bond (with  $\text{sp}^2$  hybridization). They are unstable compounds unless other groups such as carbonyl (CO), carboxyl ( $\text{COOH}$ ), or nitro ( $\text{NO}_2$ ) are bound to the other carbon connected to the double bond. Even in many stabilized compounds a keto–enol equilibrium is common:



Among a few compounds containing stabilized enol groups are ascorbic acid and 3-hydroxymethylene-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (hydroxymethylene camphor):



ascorbic acid



hydroxymethylene camphor

Being unstable compounds, enols are either impossible to isolate, or in stabilized molecules, easily decomposed by heat. For example, hydroxymethylene camphor can be distilled in vacuum but at higher temperatures undergoes condensations and decompositions into complex mixtures. Pyrolysis of ascorbic acid is discussed in Section 19.3.

## 9.3. PHENOLS

### General aspects

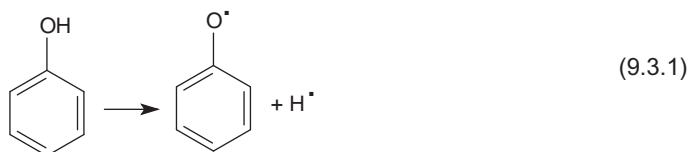
Phenols (hydroxybenzenes) are compounds with the OH group attached to a carbon that is part of an aromatic ring (the ring not including heteroatoms) and are sometimes indicated as  $\text{Ar}-\text{OH}$ . The name of the class comes from its first member, phenol. Besides phenols with one hydroxy group, compounds with more than one OH group on the aromatic ring also are well known. In this category are dihydroxybenzenes (e.g. resorcinol, catechol, and hydroquinone), trihydroxybenzenes, etc. In addition to phenols with a single aromatic ring, compounds with the OH group(s) attached to structures with two or more condensed aromatic rings are known (e.g. hydroxynaphthalenes, also known as naphthols).

The compounds with the OH group attached to an aromatic heterocycle are not considered phenols (e.g. hydroxypyridine is not a phenol).

In addition to the OH groups, other substituents can be attached to the same aromatic ring. These substituents may be of hydrocarbon type when the resulting compounds are still considered simple phenols. When the substituents consist of other functional groups (Cl, Br, NH<sub>2</sub>, COOH, etc.), they generate multifunctional compounds, which will be discussed in separate sections.

### Monohydroxybenzenes

Phenol (C<sub>6</sub>H<sub>5</sub>OH) has a high thermal stability. Only above 650 °C does the compound start decomposing to a noticeable level, and around 800 °C the decomposition occurs rapidly. The calculated variation in the mol % of remaining phenol from pyrolysis at different temperatures with a 10 s heating time is shown in Figure 9.3.1. The main pyrolysis products are cyclopentadiene and CO. Smaller quantities of benzene also were found in the pyrolysate, and even lower levels of acetylene, naphthalene, methane, and methylcyclopentadiene [39]. The initiation reaction involves the formation of free radicals by the cleavage of the O–H bond [40]. This reaction can be written as follows:



The efforts done to model shock tube experimental data indicated that the reaction may continue with the addition of the hydrogen atoms to the phenoxy radicals to generate an unstable tautomeric form of phenol (C<sub>6</sub>H<sub>6</sub>O) followed by CO abstraction [41,42]. The correct structure of this tautomeric form was difficult to assess [43,44]. It is also possible that the phenoxy radical eliminates CO directly and changes into a more stable cyclopentadienyl radical:

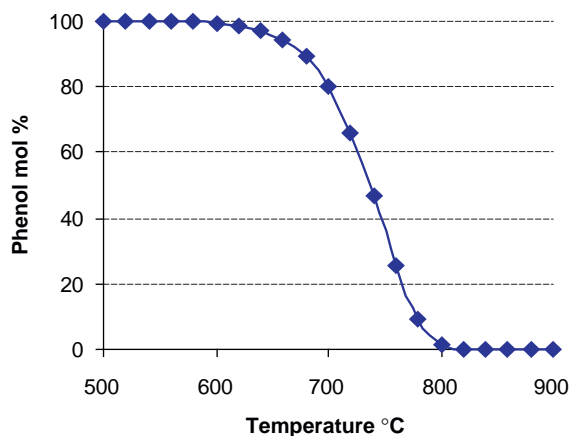
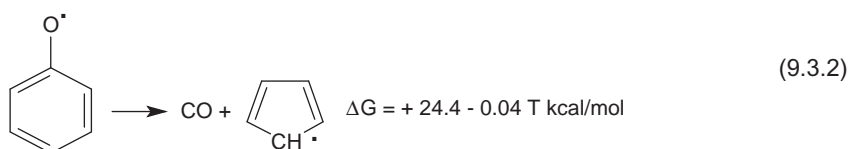
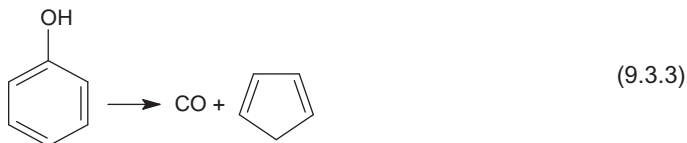


FIGURE 9.3.1. Calculated mol % of remaining phenol for pyrolysis at different temperatures with a 10 s heating time.

The reaction becomes exothermic above 340 °C and therefore is thermodynamically favorable in the conditions of phenol pyrolysis. Cyclopentadienyl radical generates cyclopentadiene by termination reaction with a  $\text{H}^\bullet$  atom or by hydrogen abstraction from a different phenol molecule. The global reaction can be written as follows:



The benzene formation from phenol is very likely the result of a reaction of the type:



Fragmentation of phenol with the formation of cyclopentadiene is similar to the formation of the fragment with  $m/z = 66$  in the mass spectrum of phenol (in standard +EI conditions). Phenol mass spectrum is shown in Figure 9.3.2 (see Section 2.3 for a discussion on similarity between fragmentation in pyrolysis and in mass spectrometry).

The fragment with  $m/z = 66$  corresponds to the ion resulting from cyclopentadiene  $\text{C}_5\text{H}_6^+$ . The reaction rate of initial phenol decomposition is described by the following Arrhenius equation:

$$k = 10^{12} \exp\left(\frac{-30600}{T(^{\circ}\text{K})}\right) \text{ s}^{-1} \quad (9.3.5)$$

The resulting cyclopentadiene from pyrolysis continues the process of decomposition with the formation of other fragments (see Section 7.5). This process also leads to the formation of PAHs (see e.g. reaction 7.5.5). Since phenol formation is believed to play an important role in the combustion of aromatic hydrocarbons (see Section 7.7), the formation of cyclopentadiene from the pyrolysis of phenol is considered one of the mechanisms acting for the formation of PAHs in the flames of aromatics.

Pyrolysis of phenol in the presence of oxygen was studied also [39]. In the presence of oxygen, the following reaction plays an important role in the formation of free radicals:



A first result of reaction 9.3.6 is an increased rate of phenol consumption during phenol pyrolysis in the presence of oxygen as compared to pyrolysis in an inert atmosphere. This increase in the decomposition rate is caused by the formation of additional phenoxy radicals as well as of  $\text{OOH}^\bullet$ .

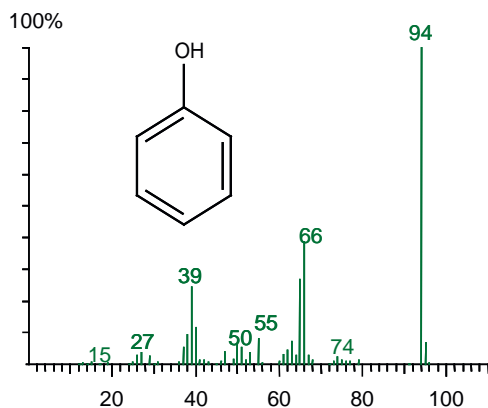
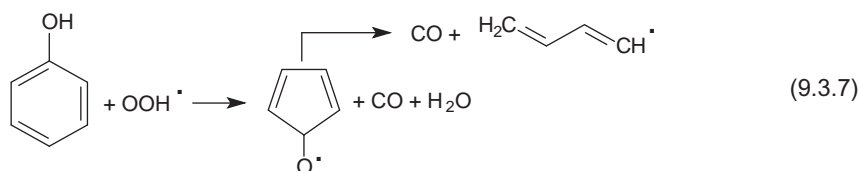


FIGURE 9.3.2. Mass spectrum of phenol.

radicals, which continue the decomposition reactions. In the presence of oxygen, the same main products as from pyrolysis in inert atmosphere are generated from phenol. However, some  $\text{CO}_2$  and low levels of  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ , several  $\text{C}_3$  hydrocarbons, and 1,3-butadiene are formed as a result of the excess of oxygen. Butadiene and the other small linear hydrocarbons are not seen in phenol pyrolysis in the absence of oxygen. The modification of the pyrolysis process in the presence of oxygen takes place by reactions of the type shown below:

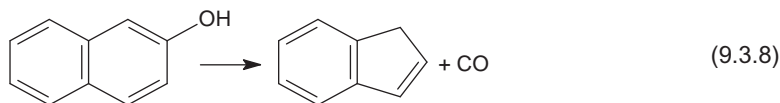


The formation of 1,3-butadienyl radical is the source of butadiene and possibly of other short-chain hydrocarbons seen when the oxygen is present [45].

Other monohydroxybenzenes, having hydrocarbon type substituents on the benzene ring, also are resistant to heating and form only a few fragments by pyrolysis [44,46,47]. One common result of pyrolysis for these compounds is the cleavage of the C–C bond between one aromatic carbon and the aliphatic one. *m*-Cresol, for example, forms some phenol and benzene by pyrolysis above 750 °C. 2,6-Bis-(1,1-dimethylethyl)-4-methylphenol (BHT) generates 2-(1,1-dimethylethyl)-4-methylphenol, while 4,4'-(1-methylethylidene)bis-phenol (Bisphenol A) generates some *p*-isopropenylphenol and some phenol, both parent compounds being very resistant to heating.

### Naphthols

Both 1-naphthol and 2-naphthol are very resistant to heating. The main pyrolysis product at temperatures above 800 °C is indene (MW = 116). The pyrolysis reaction is similar to that for phenol and can be written as follows:



Both 1-naphthol and 2-naphthol behave similarly. The fragment ions with  $m/z = 116$  and  $m/z = 115$ , corresponding to the ions  $\text{C}_9\text{H}_8^+$  and  $\text{C}_9\text{H}_7^+$ , are shown also in the mass spectrum of naphthols, proving some similarity between pyrolysis and fragmentation in mass spectrometry. The mass spectrum of 2-naphthol is shown in Figure 9.3.3.

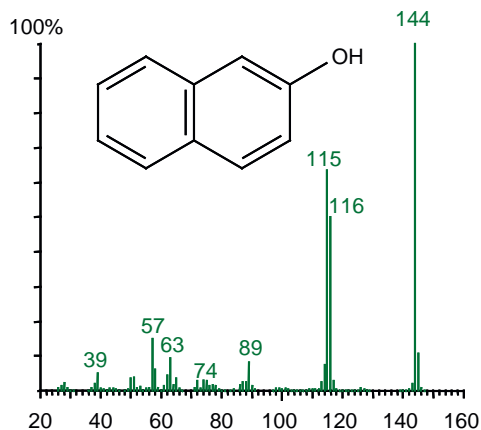


FIGURE 9.3.3. Mass spectrum of 2-naphthalenol.

At higher temperatures naphthols generate char and various levels of PAHs. As expected, naphthalene is the main aromatic compound with condensed cycles in the pyrolysate.

#### 9.4. DI- AND POLY-HYDROXYBENZENES

##### *General aspects*

The simple dihydroxybenzenes with no other functional groups attached to the benzene ring can have the OH groups attached in the positions 1,2 (catechol), 1,3 (resorcinol), and 1,4 (hydroquinone). Catechol pyrolysis was studied more frequently since this compound is considered to be related to the structure of brown coal [48] and lignin [49] and is present in biomass tars [50] and in tobacco smoke [51,52]. Most pyrolysis experiments related to these compounds were done in a flow reactor on the vapors of the parent compound and not with flash pyrolysis.

##### *Catechol*

Catechol (1,2-dihydroxybenzene  $C_6H_4(OH)_2$ ) has a fairly high thermal stability. Only above 600 °C does the compound start decomposing to a noticeable level, as shown in Figure 9.4.1, where the % of unreacted catechol and that of generated CO at different temperatures are shown. The results were obtained from an experiment in which catechol vapors at a concentration of 0.72% mol carbon in nitrogen were heated at various temperatures in a quartz flow reactor with a residence time of 0.4 s and quenching of the reaction products at room temperature [53]. Due to the relatively high volatility of the compound, flash pyrolysis performed in a pyrolyzer for solid samples does not give the same decomposition yield as shown in Figure 9.4.1.

In flash pyrolysis instruments, the catechol sample is easily volatilized and entrained by the flowing gas before reaching the decomposition temperature, and the yield of decomposed compound is lower. The pyrolysis of catechol generates compounds such as CO, benzene, phenol, cyclopentadiene, acetylene, 1,3-butadiene, and ethylene. Also, considerable levels of PAHs are formed in the reaction. The variation with temperature of the yield of main gas decomposition products of catechol (except for CO) is shown in Figure 9.4.2, and the variation in the levels of benzene, cyclopentadiene, and phenol is shown in Figure 9.4.3 [53].

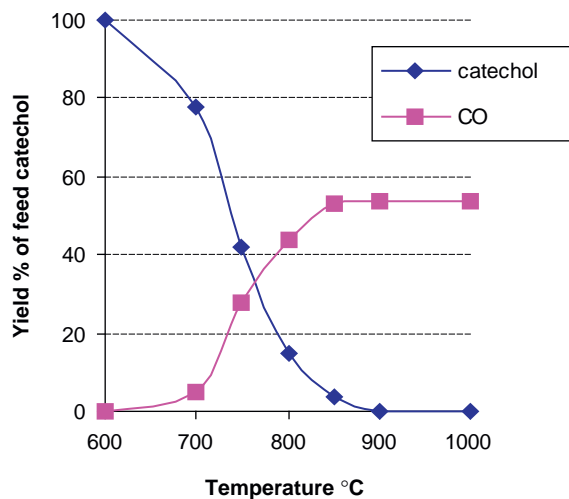


FIGURE 9.4.1. Yield % of unreacted catechol at different temperatures (0.4 s heating) and CO formation [53].

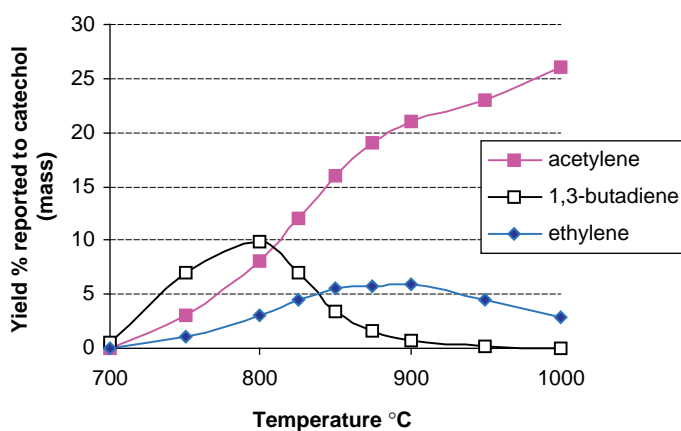


FIGURE 9.4.2. Yield % of acetylene, 1,3-butadiene, and ethylene generated from catechol decomposition at different temperatures in a flow through experiment [53].

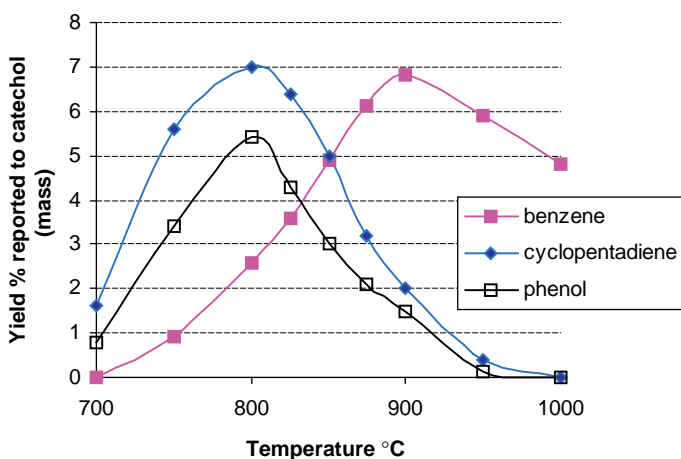


FIGURE 9.4.3. Yield % of phenol, cyclopentadiene, and benzene generated from catechol decomposition at different temperatures in a flow through experiment [53].

As shown in Figure 9.4.2, the formation of acetylene is favored by the increase in temperature, while the other molecular species have a maximum at a specific temperature and start decreasing at temperatures higher than 900 °C. The difference in the temperature profile between two pyrolysate constituents such as ethylene and acetylene is an indication that the mechanisms of their generation or decomposition are different. Other small molecules are formed at levels depending on pyrolysis temperature but not exceeding 3% of the feed catechol. These include methane (0–2.5%), ethane (0–0.3%), propyne (0–1.6%), propadiene (0–0.5%), and propylene (0–0.2%).

The reaction mechanisms for catechol pyrolysis are similar to those for phenol. The initiation reaction can be written as follows:

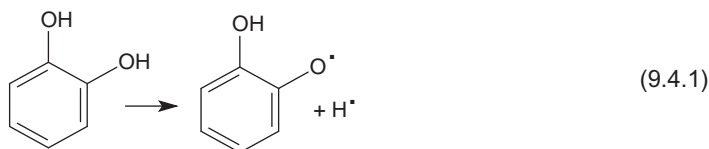
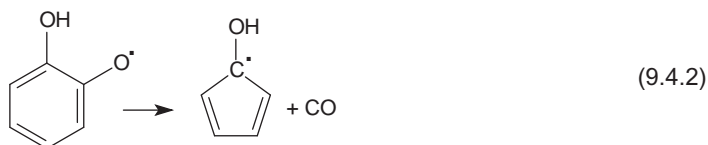


TABLE 9.4.1. Propagation and termination reactions during catechol pyrolysis

Reaction
Reactions with $\text{H}^\bullet$ radicals
$\text{C}_6\text{H}_4(\text{OH})_2 + \text{H}^\bullet \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{OH}^\bullet$
$\text{C}_6\text{H}_4(\text{OH})_2 + \text{H}^\bullet \rightarrow \text{C}_6\text{H}_4(\text{OH})\text{O}^\bullet + \text{H}_2$
$\text{C}_6\text{H}_5\text{OH} + \text{H}^\bullet \rightarrow \text{C}_6\text{H}_6 + \text{OH}^\bullet$
$\text{C}_6\text{H}_5\text{OH} + \text{H}^\bullet \rightarrow \text{C}_6\text{H}_5\text{O}^\bullet + \text{H}_2$
$\text{C}_6\text{H}_5\text{O}^\bullet + \text{H}^\bullet \rightarrow \text{C}_6\text{H}_5\text{OH}$
Reactions with $\text{OH}^\bullet$ radicals
$\text{C}_6\text{H}_4(\text{OH})_2 + \text{OH}^\bullet \rightarrow \text{C}_6\text{H}_4(\text{OH})\text{O}^\bullet + \text{H}_2\text{O}$
$\text{C}_6\text{H}_5\text{OH} + \text{OH}^\bullet \rightarrow \text{C}_6\text{H}_5\text{O}^\bullet + \text{H}_2\text{O}$

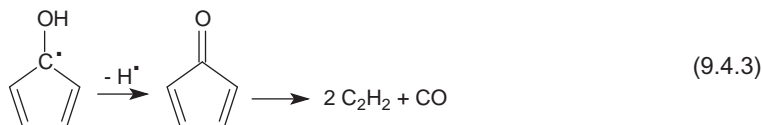
Following the formation of  $\text{H}^\bullet$ , various propagation reactions take place, as shown in Table 9.4.1. These reactions as well as some termination reactions are very likely responsible for the formation of phenol and of benzene in catechol pyrolysis. However, benzene is formed in a subsequent reaction phase after phenol is generated.

2-Hydroxyphenoxy radical  $\text{C}_6\text{H}_4(\text{OH})\text{O}^\bullet$  may eliminate CO in a reaction similar to that of phenoxy radical, as shown below:

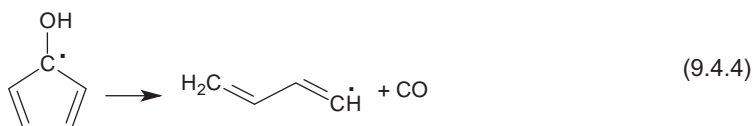


Decomposition with the intermediate formation of a tautomeric form  $\text{C}_6\text{H}_6\text{O}_2$ , similar to that proposed for the decomposition of phenol, also is possible.

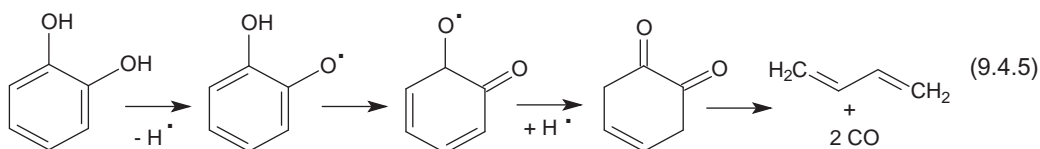
Cyclopentadienol-1-yl radical can decompose easily into cyclopentadien-5-one and  $\text{H}^\bullet$  atoms with subsequent decomposition into CO and acetylene, as shown below:



Another decomposition path for cyclopentadienol-1-yl radical is the formation of butadienyl radicals and CO, as shown below:



Reactions 9.4.3 and 9.4.4 are very likely responsible for the formation of acetylene and 1,3-butadiene, respectively, in catechol pyrolysis. Butadiene formation also may proceed through a different mechanism, having as an intermediate form a tautomer of catechol:



Additional formation of phenoxy radicals may take place (by reaction 9.3.1) from a secondary pyrolysis of phenol previously generated from catechol. Similar to the phenol case, phenoxy radicals may generate CO and cyclopentadienyl radicals that lead to the formation of cyclopentadiene [43]. Also, cyclopentadienyl radical may decompose to form propargyl radical  $C_3H_3^{\bullet}$  and acetylene.

Cyclopentadienyl radical and cyclopentadiene may react with the formation of a dimer radical ( $C_{10}H_7^{\bullet}$ ). This dimer has been shown to lead to the formation of PAHs (see Section 7.5). The presence of these precursors in catechol pyrolysate explains the high yield of PAHs. Acetylene, butadiene, and benzene also may have contribution to PAH formation. The yield of formation of PAHs with two to eight rings as a function of temperature in the flow through pyrolysis experiment previously described is shown in Figure 9.4.4 [53]. The decrease in the yield of PAHs as temperature increases beyond 950 °C is explained by the decomposition of PAH precursors, in particular of cyclopentadiene, into smaller molecules such as  $C_2H_2$  instead of undergoing condensation reactions.

Extensive studies were performed for the identification of PAHs and oxygenated PAHs in catechol pyrolysate [54–58]. Pyrolysis of catechol in the same flow through type experiment as previously described, with 0.70% mol carbon in nitrogen heated at 1000 °C in a quartz flow reactor with a residence time of 0.4 s, generated the PAHs listed in Table 9.4.2 [54].

In addition to the compounds listed in Table 9.4.2, biphenyl, 1-phenylnaphthalene, and indene were detected. Besides the formation of simple PAHs, oxygenated PAHs also are present in catechol pyrolysates. Among the oxygenated compounds with two or three cycles, benzofuran, dibenzofuran, phenalene, 9-fluorenone, and 1-naphthol were detected. Also, several alkylated aromatics as well as several aromatic compounds substituted with ethynyl radicals were detected. Among the ethynyl substituted aromatic compounds were phenylacetylene, 2-ethynylnaphthalene, 1-ethynylacenaphthylene, 5-ethynylacenaphthylene, 2-ethynylphenanthrene, 3-ethynylphenanthrene, and 2-ethynylantracene. The presence of all these compounds in catechol pyrolysate shows that catechol is a likely precursor of PAHs in the tar generated from many materials containing free or bound catechol, such as wood.

Pyrolysis of catechol in fuel-rich oxidation conditions was studied for the same reasons as pyrolysis in an inert atmosphere. Catechol is a model compound for solid fuels since it is present in biomass tar and tobacco smoke and is related to the chemical structure of lignin and brown coal. Pyrolysis results for several  $O_2$ /catechol ratios (0.22, 0.58, and 0.920) were reported [56,57]. The ratios were calculated as the mass feed rate of oxygen vs. the mass feed rate of catechol. The experiment was performed in a flow through reactor with the catechol entrained in pure nitrogen, resulting in a concentration of 0.65 mole % of carbon loading. The temperature range for the experiment was 500–1000 °C, and the residence time in the heated zone was 0.3 s. The variation in the % of catechol remaining from the initial level at different temperatures and  $O_2$ /catechol ratios is shown in Figure 9.4.5 [56].

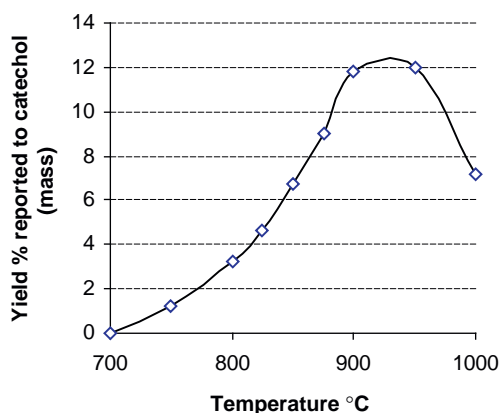


FIGURE 9.4.4. Yields % of total PAHs with two to eight rings from catechol decomposition at different temperatures in a flow through experiment [53].



TABLE 9.4.2. List of PAHs identified in catechol pyrolysate at 1000 °C [54]

	Compound	Formula
1	Naphthalene	C <sub>10</sub> H <sub>8</sub>
2	Acephenanthrylene	C <sub>12</sub> H <sub>8</sub>
3	Fluorene	C <sub>13</sub> H <sub>10</sub>
4	Benz[ <i>f</i> ]indene	C <sub>13</sub> H <sub>10</sub>
5	Phenanthrene	C <sub>14</sub> H <sub>10</sub>
6	Anthracene	C <sub>14</sub> H <sub>10</sub>
7	Pyrene	C <sub>16</sub> H <sub>10</sub>
8	Fluoranthene	C <sub>16</sub> H <sub>10</sub>
9	Aceanthrylene	C <sub>16</sub> H <sub>10</sub>
10	Benzo[ <i>a</i> ]fluorene	C <sub>17</sub> H <sub>12</sub>
11	Cyclopent[ <i>h</i> ]acephenanthrylene	C <sub>18</sub> H <sub>10</sub>
12	Cyclopenta[ <i>cd</i> ]fluoranthene	C <sub>18</sub> H <sub>10</sub>
13	Cyclopenta[ <i>cd</i> ]pyrene	C <sub>18</sub> H <sub>10</sub>
14	Benzo[ <i>c</i> ]phenanthrene	C <sub>18</sub> H <sub>12</sub>
15	Triphenylene	C <sub>18</sub> H <sub>12</sub>
16	Benz[ <i>a</i> ]anthracene	C <sub>18</sub> H <sub>12</sub>
17	Chrysene	C <sub>18</sub> H <sub>12</sub>
18	Dicyclopenta[ <i>cd,mn</i> ]pyrene	C <sub>20</sub> H <sub>10</sub>
19	Dicyclopenta[ <i>cd,jk</i> ]pyrene	C <sub>20</sub> H <sub>10</sub>
20	Benzo[ <i>e</i> ]pyrene	C <sub>20</sub> H <sub>12</sub>
21	Perylene	C <sub>20</sub> H <sub>12</sub>
22	Benzo[ <i>a</i> ]pyrene	C <sub>20</sub> H <sub>12</sub>
23	Benzo[ <i>a</i> ]fluoranthene	C <sub>20</sub> H <sub>12</sub>
24	Benzo[ <i>b</i> ]fluoranthene	C <sub>20</sub> H <sub>12</sub>
25	Benzo[ <i>j</i> ]fluoranthene	C <sub>20</sub> H <sub>12</sub>
26	Acenaphthylene	C <sub>20</sub> H <sub>12</sub>
27	Benzo[ <i>ghi</i> ]perylene	C <sub>22</sub> H <sub>12</sub>
28	Anthanthrene	C <sub>22</sub> H <sub>12</sub>
29	Indeno[1,2,3- <i>cd</i> ]pyrene	C <sub>22</sub> H <sub>12</sub>
30	Dibenz[ <i>ah</i> ]anthracene	C <sub>22</sub> H <sub>14</sub>
31	Dibenz[ <i>a</i> ]anthracene	C <sub>22</sub> H <sub>14</sub>
32	Benzo[ <i>b</i> ]chrysene	C <sub>22</sub> H <sub>14</sub>
33	Picene	C <sub>22</sub> H <sub>14</sub>
34	Coronene	C <sub>24</sub> H <sub>12</sub>
35	Benzo[ <i>ghi</i> ]cyclopenta[ <i>cd</i> ]perylene	C <sub>24</sub> H <sub>12</sub>
36	Naphtho[1,2- <i>a</i> ]pyrene	C <sub>24</sub> H <sub>14</sub>
37	Naphtho[2,3- <i>a</i> ]pyrene	C <sub>24</sub> H <sub>14</sub>
38	Dibenzo[ <i>a</i> ]pyrene	C <sub>24</sub> H <sub>14</sub>
39	Cyclopenta[ <i>bc</i> ]coronene	C <sub>26</sub> H <sub>12</sub>
40	Dibenzo[ <i>cd,m</i> ]perylene	C <sub>26</sub> H <sub>14</sub>
41	Phenanthreno[2,3- <i>a</i> ]pyrene	C <sub>28</sub> H <sub>16</sub>

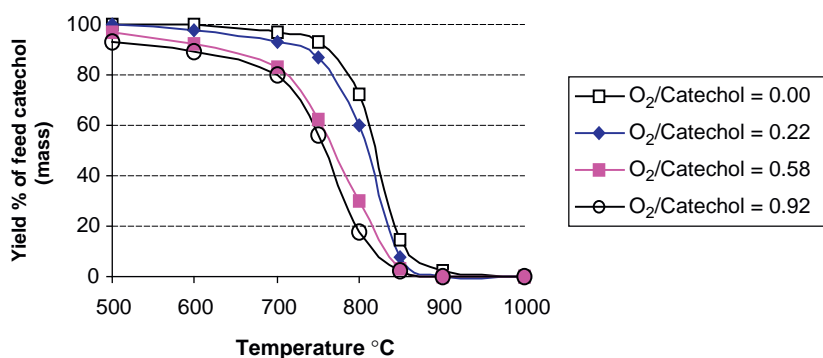


FIGURE 9.4.5. Yields % of feed catechol remaining from the initial level at different temperatures and oxygen/catechol ratios in a flow through experiment [56].

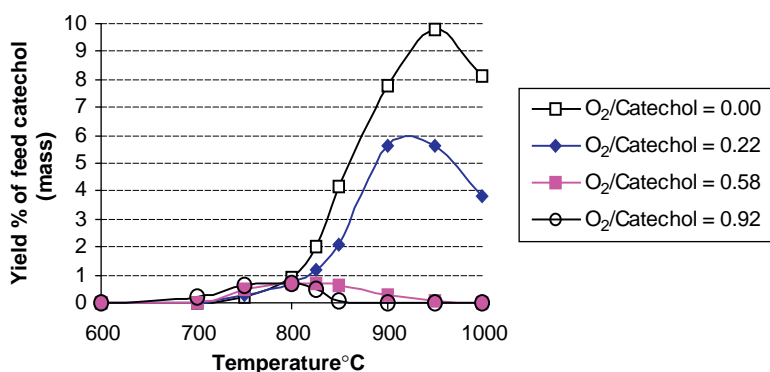
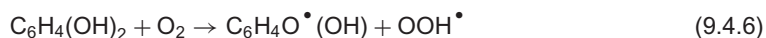


FIGURE 9.4.6. Yields % of total PAHs with two to eight rings from catechol decomposition at different temperatures in the presence of oxygen at different O<sub>2</sub>/catechol ratios in a flow through experiment [57].

Similar to the case of phenol pyrolysis in the presence of oxygen, the rate of catechol consumption in the presence of oxygen is higher than in pyrolysis in an inert atmosphere. The following reactions are caused by the presence of oxygen:



The main reaction products of oxidative pyrolysis of catechol are not different from those generated in the absence of oxygen, except for CO<sub>2</sub>, which is formed only when oxygen is present. The compounds include CO, CO<sub>2</sub>, methane, ethane, ethylene, acetylene, propyne, propylene, propadiene, 1,3-butadiene, vinylacetylene, cyclopentadiene, phenol, benzene, toluene, styrene, phenylacetylene, and a considerable number of PAHs [57]. As the O<sub>2</sub>/catechol ratio increases, the yields of most compounds have a tendency to have a maximum at lower temperatures. The shift for the O<sub>2</sub>/catechol = 0.92 compared to pyrolysis in an inert atmosphere was between 100 °C and 150 °C. In addition to the optimum temperature shift, many compounds were generated at lower levels (exceptions being CO, CO<sub>2</sub>, C<sub>2</sub>, and C<sub>3</sub> hydrocarbons). A significant decrease in the production of PAHs also was seen as the ratio O<sub>2</sub>/catechol increases. This decrease is shown in Figure 9.4.6 for the total level of PAHs with two to eight rings.

Variations in the yield of individual PAHs with temperature and O<sub>2</sub>/catechol ratio were described in the literature [57]. Although differences were seen from one individual PAH to another, the general trend

is similar to that of global variation shown in Figure 9.4.6. Oxidative pyrolysis of catechol also was studied with nanoparticles of iron oxide as a solid support, which may simulate the presence of ash during burning and may act as a catalyst [55]. The decomposition of catechol in the presence of iron oxide occurs at lower temperatures, and indanone is formed as a new compound in the pyrolysate.

Pyrolysis of 3-methylcatechol is very similar to that of catechol. However, besides other decomposition products, benzene is detected in the pyrolysate but no toluene. Resorcinol is expected to generate by pyrolysis compounds similar to those of catechol.

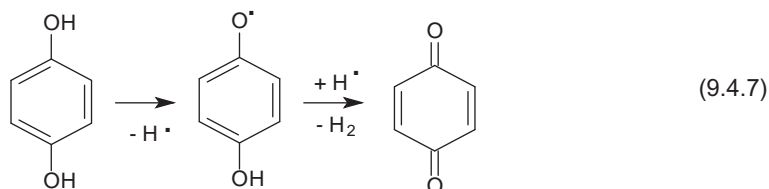
### Hydroquinone

Hydroquinone is present in biomass tar and in tobacco smoke, resulting probably from the pyrolysis of lignin type materials. Pyrolysis of hydroquinone is of concern not only because of the formation of PAHs, dibenzofuran, and dibenzo-*p*-dioxin, but also due to the potential formation of persistent free radicals such as *p*-semiquinone [59].

Hydroquinone is not as stable to heating as catechol. Pyrolysis of hydroquinone was studied in a flow reactor with a residence time of 2 s [59]. Below 650 °C the main pyrolysis product is benzoquinone, with a maximum yield of about 15% from the hydroquinone feed at 500 °C. Above 700 °C substituted aromatic compounds were formed, including phenol (maximum yield of 6% at 775 °C). Low levels of other compounds included benzene (maximum yield of 0.2% at 900 °C), styrene (maximum yield of 0.4% at 900 °C), indene (maximum yield of 0.1% at 850 °C), naphthalene (maximum yield of 0.1% at 900 °C), biphenylene (maximum yield of 0.2% at 850 °C), and phenylethyne (maximum yield of 0.04% at 900 °C). Dibenzofuran was detected in the temperature range from 725 °C to 1000 °C with a maximum yield of 1% at 775 °C. Dibenzo-*p*-dioxin also was detected, with a maximum yield of 0.4% at 775 °C in the temperature range from 725 °C to 950 °C [59].

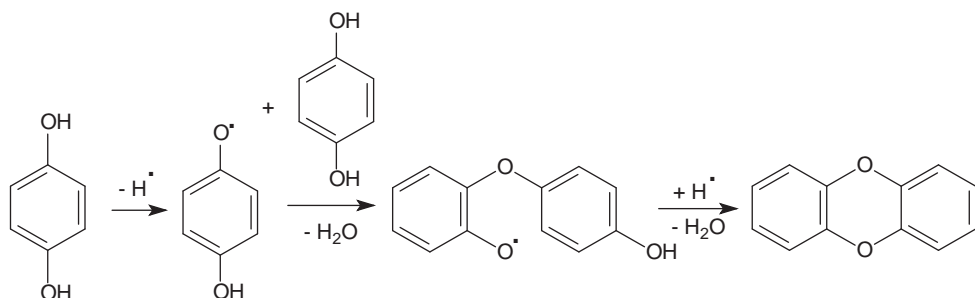
Pyrolysis of hydroquinone also was performed in the presence of isopropyl alcohol as a source of hydrogen [59]. The addition of a hydrogen source was intended to simulate the conditions in a fuel-rich flame where sources of hydrogen are available. The presence of isopropyl alcohol generates hydrogen above 600 °C (see reaction 9.1.9) and affects the hydroquinone pyrolysis process. In the presence of the hydrogen source, below 650 °C the main pyrolysis product of hydroquinone is benzoquinone. The maximum yield of this compound is about 33% at 550 °C. The formation of hydrogen atoms from the alcohol pyrolysis probably increases the abstraction of hydrogens from the OH groups of hydroquinone to generate a higher yield of benzoquinone compared to pyrolysis in an inert atmosphere. In the presence of isopropyl alcohol, some phenol also is formed at about 2% level, with a maximum at 700 °C. Above 700 °C, higher yields of substituted aromatic compounds were noticed. These included styrene (maximum yield of 15% at 850 °C), indene (maximum yield of 2% at 850 °C), naphthalene (maximum yield of 2% at 925 °C), biphenylene (maximum yield of 6% at 900 °C), and phenylethyne (maximum yield of 2% at 950 °C). Dibenzofuran was detected in the narrow temperature range from 800 °C to 900 °C with a maximum yield of 0.2% at 850 °C, but the formation of dibenzofuran is drastically reduced, and dibenzo-*p*-dioxin is not detected in the presence of isopropanol [59].

Pyrolysis of hydroquinone starts with an initiation reaction similar to that for phenol and catechol. The stability of *p*-benzoquinone favors a continuation of the initiation reaction as shown below:



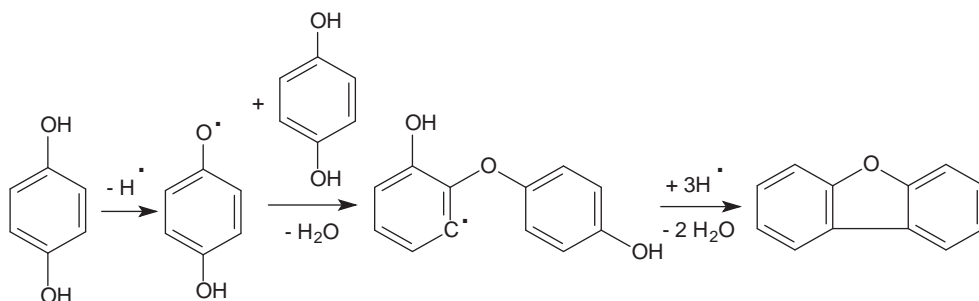
The formation of *p*-semiquinone free radical during hydroquinone pyrolysis is of particular concern since this free radical is comparatively stable. Various studies were performed on the formation of *p*-semiquinone free radical during pyrolysis processes, particularly in cigarette smoke [60,61].

Other pyrolysis products including PAHs are generated by mechanisms very similar to those described for catechol. The process of formation of dibenzofuran and dibenzo-*p*-dioxins appears to have a higher yield in case of hydroquinone pyrolysis as compared to catechol or even phenol. Therefore a mechanism involving a phenoxyl radical [59] does not explain this process. The following sequence of reactions, which does not involve the formation of *p*-benzoquinone as an intermediate species, may explain the formation of dibenzo-*p*-dioxin:



(9.4.8)

The formation of dibenzofuran can follow a similar path, as shown below:



(9.4.9)

The presence of the OH electron-donor substituents on the benzene ring may have a stabilizing effect on the intermediate free radicals formed during this process. In a similar way, the formation of dioxins and halogenated dioxins from halogenated phenols is favored by the presence of the electron donor halogen substituents on the aromatic ring (see Section 9.5). However, the precise mechanism (or mechanisms) of the formation of these compounds is not yet established, and various alternative paths are described in the literature [59].

Pyrolysis of 2,3-dimethylhydroquinone generates mainly 2,3-dimethyl-*p*-benzoquinone (2,3-dimethyl-2,5-cyclohexadien-1,4-dione) and 2,3-dimethylphenol, as well as low levels of toluene. The C–C bond between the alkyl groups and the aromatic ring is relatively stable in the parent molecule.

### Other phenols

Simple phenols have molecules typically stable to heating. Even trihydroxybenzenes (pyrogallol with 1,2,3 substitution, phloroglucinol with 1,3,5 substitution, and hydroxyhydroquinone with 1,3,4 substitution) are stable upon heating, and they are present in the pyrolysates of other related compounds such as gallic acid, various phenolic ethers, or complex materials such as lignin, tannins, and humic acids [49]. For example, chebulinic acid, which is a hydrolyzable tannin, contains four pyrogallol moieties. Upon pyrolysis, pyrogallol is formed along with other fragments. Pyrolysis results from this type of material are reported frequently in the literature [49,62,63]. Formation of phenols in various pyrolytic processes may be associated with some health issues, since some phenols are biologically active compounds [64]. Formation of phenols in specific burning processes, e.g. of plant materials, are reported in the literature [65].

### Metallic derivatives of phenols

Phenols have a slight acidic character (e.g. phenol itself has a  $pK_a = 9.9$ ) and can form combinations with metals known as phenoxides (phenolates). Phenoxides are typically less stable to heating compared to the phenols, but more stable compared to alcoxides. Sodium phenoxide starts with a slight decomposition around 400 °C and decomposes much faster around 500 °C. The decomposition products consist of small molecules such as carbon,  $H_2$ ,  $CH_4$ ,  $C_2H_6$ , and  $C_2H_4$ , some benzene and phenol, and lower levels of condensation products such as biphenyl, diphenyl ether, hydroxy-diphenyl, and dihydroxydiphenyl. The inorganic salt  $Na_2CO_3$  also is generated from pyrolysis.

## 9.5. ALCOHOLS AND PHENOLS WITH ADDITIONAL FUNCTIONAL GROUPS

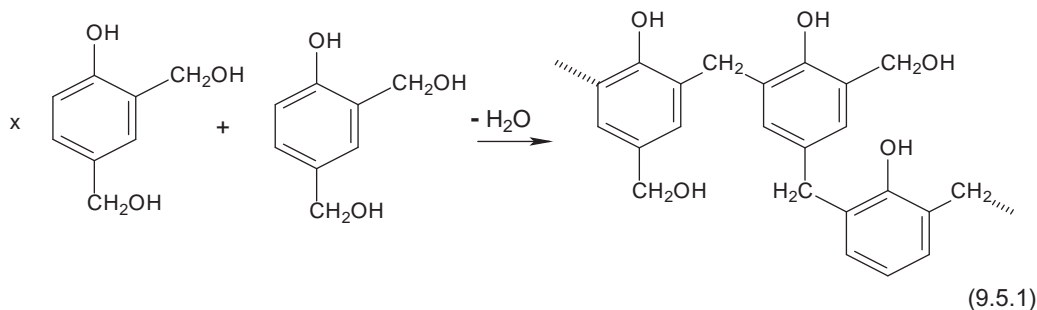
### General aspects

A large number of natural or synthesized compounds contain in their molecule phenolic OH groups and other functional groups. In this section, the discussion will be limited to compounds with phenol and alcohol groups and compounds having phenol and halogen groups. The compounds with phenol and alcohol groups are common in nature. For example, many lignin precursors (monolignols) have phenol and alcohol groups in the molecule. Among these, *p*-coumaryl alcohol or 4-(3-hydroxy-1-propenyl)phenol and syringyl alcohol or 4-(hydroxymethyl)-3,5-dimethylphenol contain only phenol and alcohol groups, while coniferyl and sinapyl alcohols in addition have methoxy groups attached to the phenolic ring. Estradiol and estriol, which are among the main estrogens produced by the human body, contain one phenolic and one or two alcohol groups, respectively, in the molecule. Besides natural compounds, the synthetic polymer Bakelite is generated in a thermal reaction involving hydroxymethylphenol. Halogenated phenols are synthetic compounds frequently used as pesticides (e.g. 2,4,6-trichlorophenol, also used as an antiseptic), and their pyrolysis is of considerable concern due to the generation of halogenated dibenzo-*p*-dioxins and halogenated dibenzofurans.

### Phenols with alcohol groups

As previously discussed for the pyrolysis of alcohols and phenols, the alcohol groups are somewhat less resilient to heating compared to phenols. For this reason, during pyrolysis of compounds containing both these functional groups, it is expected that reactions typical for alcohols would occur at lower temperatures and with higher rates than those for phenolic OH groups. Pyrolysis of model compounds with phenolic OH groups also having OH alcohol groups is relevant, particularly for the understanding of the composition of pyrolysates of lignins. Since most monolignols also contain ether groups, the subject will be discussed further in Section 10.4.

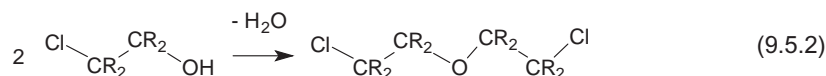
The phenols containing one or more  $CH_2-OH$  groups attached to the benzene ring are of particular interest for the production of thermosetting phenolic resins (Bakelite). The hydroxymethylphenols are generated from the reaction of phenol and formaldehyde in various conditions (basic or acidic). Upon heating, the typical reaction of monomeric molecules is water elimination, as shown in the following reaction:



Formaldehyde elimination also is possible, the end result being the same polymeric material. Pyrolysis results for this polymer are described in the literature [66].

### Alcohols with halogen groups

The presence of a halogen in  $\alpha$ ,  $\beta$ ,  $\gamma$ , etc. position to the OH group in the molecule of an alcohol leads to compounds known as halohydrins (chlorhydrins when the halogen is chlorine).  $\alpha$ -Chlorhydrins are not stable compounds, easily eliminating HCl.  $\beta$ -Chlorhydrins are typically obtained from an alkene and hypochlorous acid (HOCl). These compounds usually decompose generating halogenated ethers as shown below:



Further decomposition reactions are likely, depending on temperature and the nature of the substituents R. The bond energy X-C for X = F, Cl, Br, I in X-CH<sub>2</sub>CH<sub>2</sub>OH has been reported in the literature [67].

### Phenols with halogen groups

The main interest in pyrolysis of halogenated phenols is related to the formation of halogenated dibenzo-*p*-dioxins (dioxins) and halogenated dibenzofurans (furans) [68]. Halogenated phenols are produced as a by-product during paper manufacturing when bleaching is done with chlorine and/or Ca(OCl)<sub>2</sub>. Brominated phenols are used as flame retardants (e.g. tetrabromo-bisphenol A). Because of the concern related to the generation of dioxins and furans by the paper industry and by the incineration of paper containing traces of chlorine, considerable effort has been invested in finding alternative ways of bleaching the paper without the use of chlorine (see e.g. [69]). Pyrolysis of flame retardants was the subject of various studies because of the same concern [70].

Several studies were performed on model compounds such as 2-chlorophenol [71], 2-bromophenol [72], 2,4,6-trichlorophenol [73], and 2,4,6-tribromophenol, [74]. 2-Chlorophenol and 2-bromophenol were evaluated at temperatures between 300 °C and 950 °C as separate compounds [71,72] as well as in a mixture [75]. The experiments were performed in a flow reactor connected online with a GC/MS system. The parent compounds were injected in a flow of He at 280 °C, maintaining a 90-ppm concentration in the gas phase. Individual compounds behaved somewhat differently when pyrolyzed separately than when they were pyrolyzed in a mixture. For the experiments performed on individual parent compounds, the decomposition as a function of temperature is shown in Figure 9.5.1.

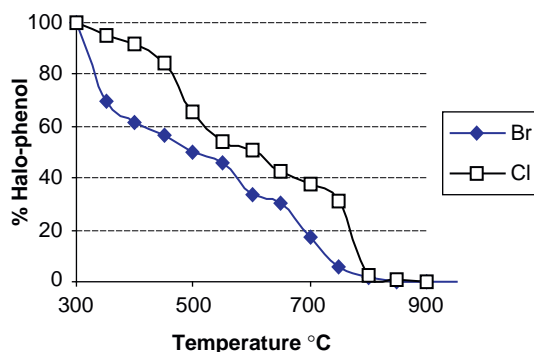


FIGURE 9.5.1. % 2-Chlorophenol and % 2-bromophenol remaining in the pyrolysate at different temperatures [71,72].

As shown in Figure 9.5.1, 2-bromophenol decomposes slightly more easily than 2-chlorophenol. Both compounds generate by pyrolysis naphthalene, chloronaphthalene, and bromonaphthalene (respectively), acenaphthalene, phenol, benzene, chlorobenzene and bromobenzene (respectively), phenylethyne, and diphenylethyne. 2-Bromobenzene also generates some 2,4-dibromophenol and 2,6-dibromophenol. Gaseous compounds such as  $H_2$ ,  $CO$ , and  $H_2O$  also were formed. One interesting difference between the two compounds was that 2-chlorophenol eliminated mainly  $HCl$ , while 2-bromophenol eliminated mainly  $Br_2$ .

Particularly important for the pyrolysis of halogenated phenols is the formation of dioxins and furans. Both nonhalogenated dibenzodioxin and dibenzofuran are generated by pyrolysis of 2-halogenophenol, the results being shown in Figures 9.5.2 and 9.5.3 [71,72].

One of the possible mechanisms for formation of dibenzodioxin from 2-bromophenol is shown below:

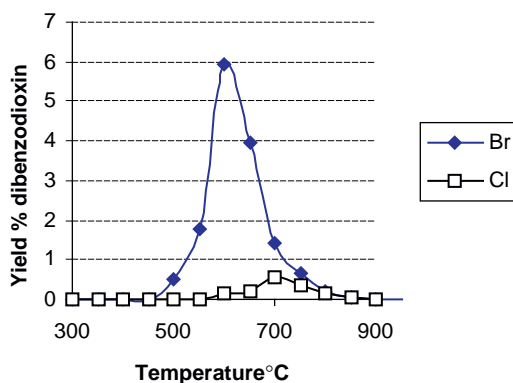
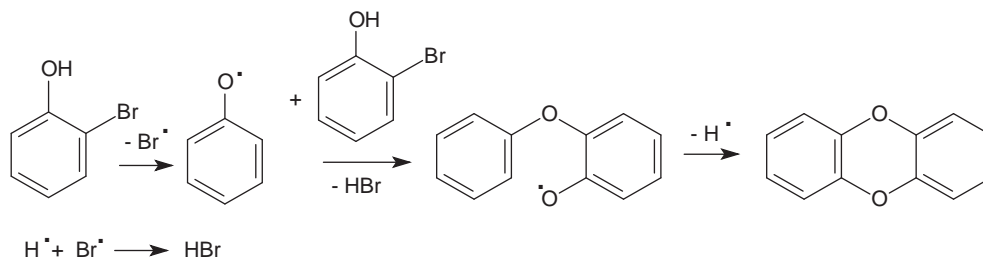


FIGURE 9.5.2. Yield % of dibenzodioxin from 2-halogenophenol [71,72].

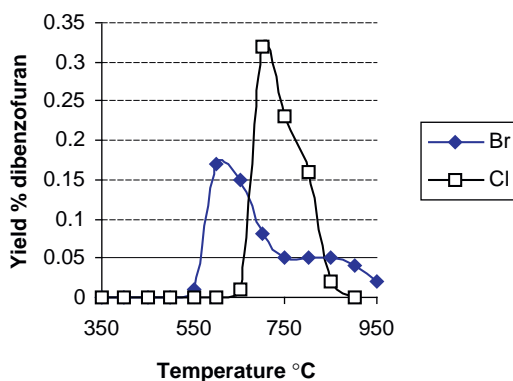
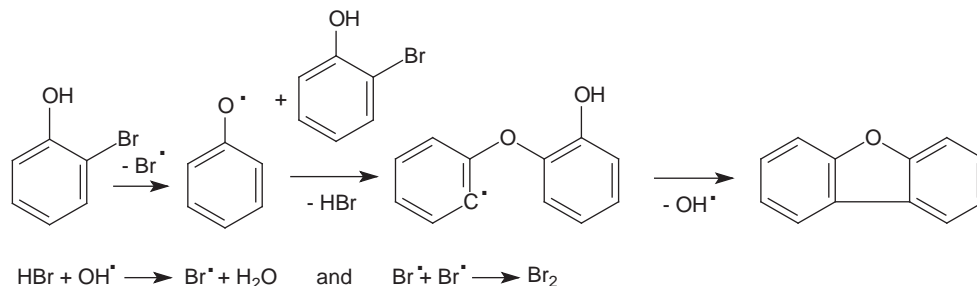


FIGURE 9.5.3. Yield % of dibenzofuran from 2-halogenophenol [71,72].

Similarly, dibenzofuran can be formed as a result of the following reactions:



Although not dangerous by themselves, dibenzodioxins and dibenzofurans are still compounds of concern. "De novo" halogenation processes can occur easily in complex mixtures where the halogens can be generated from other sources, leading to the formation of toxic halogenated dioxins and furans.

Pyrolysis of 2-halogenophenols also generates directly 1-chlorodibenzodioxin (from the 2-chlorophenol) and 1-bromodibenzodioxin and 4-bromodibenzofuran (from 2-bromophenol). The variation with temperature in the yield of these compounds is shown in Figures 9.5.4 and 9.5.5.

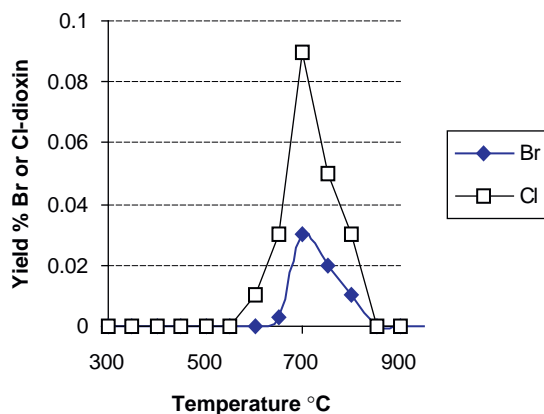


FIGURE 9.5.4. Yield % of halogenodibenzodioxin from 2-halogenophenol [71,72].

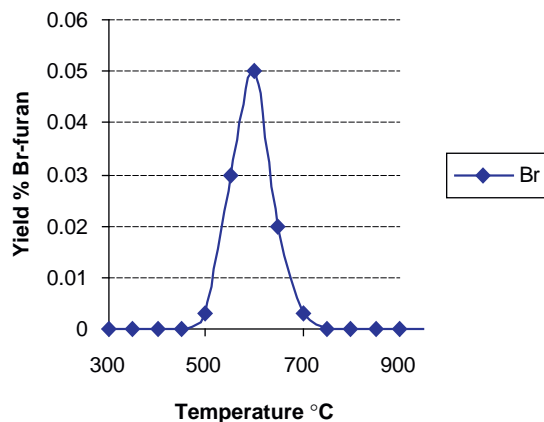
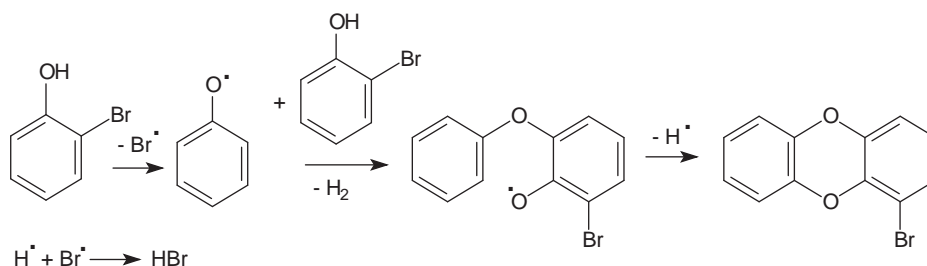


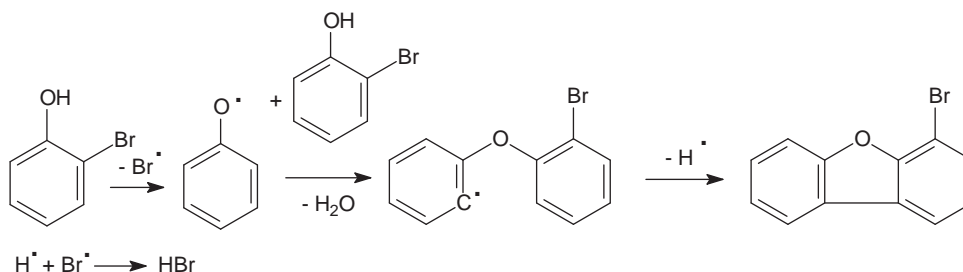
FIGURE 9.5.5. Yield % of bromo-dibenzofuran from 2-bromophenol [71,72].



One of the possible mechanisms for formation of 1-bromodibenzodioxin from 2-bromophenol is shown below:

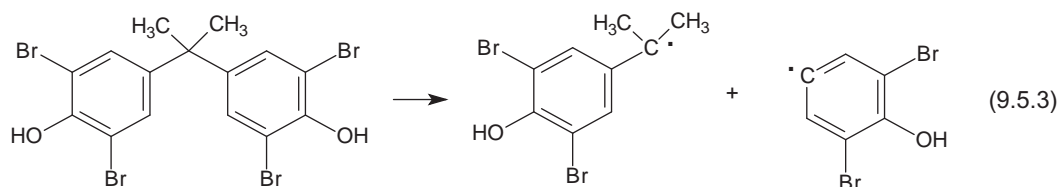


Similarly, 4-bromodibenzofuran can be formed as a result of the following reactions:



A study similar to that performed on individual 2-halogenophenol was performed on a mixture of the two compounds [75], proving the influence of one compound on the other in a free radical process. Other studies evaluated the kinetic parameters for the generation of dioxins during the pyrolysis of chlorinated phenols in gas phase [76], evaluated the formation of dioxin from chlorophenol or bromophenol by pyrolysis in the presence of solid supports (catalysts) such as CuO [77] and CuO/Silica [78,79], and studied the pyrolysis of tetrabromobisphenol A [80,81]. The interest in thermal decomposition of tetrabromobisphenol A is caused by the use of this compound as a flame retardant, mainly added to plastics. This compound begins decomposing around 200 °C. In the range 200–500 °C, it generates CO, HBr, brominated phenols, condensation compounds with dioxin type structures, and char. The thermal degradation of tetrabromobisphenol A occurs mainly in condensed phase. The flame retardation is a complex process caused by the generation of noncombustible HBr and also by the charring process that forms compact surfaces with little access for the external oxygen. The main reaction types occurring in tetrabromobisphenol A pyrolysis are indicated in Table 9.5.1. A multitude of reactions of the type described in Table 9.5.1 were considered in a kinetic model that provided parameters able to describe satisfactory thermogravimetric data and provided guidance regarding the potential distribution of pyrolysis products, including brominated dibenzodioxins and brominated dibenzofurans [81].

In addition to reactions initiated by  $\text{Br}^\bullet$  radical formation, a C–C bond can be achieved in reactions as shown below:



The free radicals generated in reaction 9.5.3 lead to the formation of bromophenols and bromobenzene, which contribute to the formation of brominated dibenzofurans and dibrominated dibenzodioxins [68,82].

TABLE 9.5.1. *Potential reactions during tetrabromobisphenol A pyrolysis*

Initiation reaction with Br <sup>•</sup> radicals formation
Unimolecular from tetrabromobisphenol A
Bimolecular from tetrabromobisphenol A
Unimolecular from heavy condensates during char formation
Propagation reaction
H <sup>•</sup> abstraction R <sup>•</sup> + R <sub>1</sub> H → RH + R <sub>1</sub> <sup>•</sup> of <i>n</i> -propyl or phenoxy hydrogen
Addition of phenoxy radicals
Bromine radical addition and cleavage
Radical intramolecular addition and Br <sup>•</sup> elimination
CO elimination from radicals
β-Decomposition of radicals
Radical addition to double bonds
Termination reaction
Br <sup>•</sup> + Br <sup>•</sup> → Br <sub>2</sub>
Large radicals recombination
Large radicals + – Br <sup>•</sup>
Molecular reaction
HBr elimination (concerted path)
H <sub>2</sub> O elimination (concerted path)

In reactions similar to those for 2-chlorophenol and 2-bromophenol, pyrolysis of 2,4,6-tribromophenol and of 2,4,6-trichlorophenol generate halogenated dibenzo-*p*-dioxins [83,84]. Among other pyrolysis products, the pyrolysate of a mixture of 2,4,6-tribromophenol and 2,4,6-trichlorophenol generates both tetrabromo- and tetrachloro-dibenzo-*p*-dioxins as well as compounds with mixed halogens. In the pyrolysate of equimolecular mixture of the two parent compounds, the most abundant congeners were dibromo-dichlorodibenzo-*p*-dioxins. The formation of tetra-(bromochloro)dibenzo-*p*-dioxins indicated that more chlorinated dioxins were produced at lower temperatures, and more brominated dioxins were formed at higher temperatures.

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## CHAPTER 10

*Pyrolysis of Ethers***10.1. ALIPHATIC ETHERS*****General aspects***

Ethers are compounds with the general formula  $R-O-R'$ , where  $R$  and  $R'$  are hydrocarbon radicals. The radicals  $R$  and  $R'$  can be aliphatic, aromatic, unsaturated (with the carbon atom connected to the oxygen atom involved in a double bond), or combinations of the three previous possibilities. The common name of ethers is derived from the two groups  $R$  and  $R'$  (in alphabetical order) by adding the word *ether* or using the prefix *di-* when  $R$  and  $R'$  are identical. The IUPAC name considers the  $OR$  group as a substituent (alkoxy or phenoxy) attached to the (larger) radical. Ethers can have one ether group in their molecule, such as diethyl ether  $C_2H_5-O-C_2H_5$ , or more ether groups, such as dimethoxyethane  $CH_3-O-C_2H_4-O-CH_3$ . Some ethers have a cyclic structure, common examples being dioxane and tetrahydrofuran. Epoxides are cyclic ethers containing a three-atom ring. Ether bonds are also present in acetals (and ketals) and hemiacetals. Acetals are generated from an aldehyde (or ketone) and two molecules of an alcohol by elimination of water and formation of two ether bonds to the same carbon atom (from the carbonyl group). Hemiacetals are generated from an aldehyde (or ketone) and one molecule of an alcohol, with formation of one ether bond and an  $OH$  group to the same carbon atom (from the carbonyl group). Thermal decomposition of each ether type has its own characteristics, which are described further in this chapter.

In cyclic form, carbohydrates (saccharides, sugars) can also be considered hemiacetals. They contain the  $C-O-C$  moiety besides several  $OH$  groups. Many anhydro sugars also contain additional ether groups (e.g., levoglucosan). These compounds are not presented in this chapter, the pyrolysis of saccharides being discussed in Chapter 16. Also, furans and pyrans are examples of other compounds that contain the typical  $C-O-C$  ether group in the molecule. However, these compounds are classified as aromatic heterocycles, and their pyrolysis is discussed in Chapter 21.

***Ethers with short carbon chains***

Aliphatic ethers with a short carbon chain have various practical applications such as solvents, aerosol spray propellants, intermediates in chemicals synthesis, etc. Pyrolysis of ethers with oxygen bonded to at least one primary or secondary carbon has the tendency to generate aldehydes or ketones, and a hydrocarbon. However, this rule is not always obeyed. The typical reaction can be written as follows:



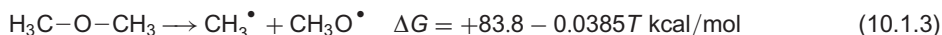
Dimethyl ether, for example, when heated above  $500^\circ C$  forms methane and formaldehyde, with the further decomposition of formaldehyde into  $CO$  and  $H_2$ , as shown in the following reactions:



Dimethyl ether has a high cetane number (CN). The CN is a measurement of the combustion quality of a diesel fuel during compression ignition. For a tested fuel, CN is defined as the percentage (v/v) of *n*-hexadecane (cetane) in a mixture with 1-methylnaphthalene that produces a fuel with the same ignition characteristics (ignition delay) as the tested fuel. The combustion should be performed in a standard engine under specified operating conditions. Pure *n*-hexadecane has  $CN = 100$ . A fuel with higher CN has shorter ignition delay periods than lower cetane fuels. Having a high CN, although it has

a boiling point (b.p.) of  $-23^{\circ}\text{C}$ , dimethyl ether was evaluated as an alternative diesel fuel. For this reason, pyrolysis and oxidative pyrolysis of the compound received special attention [1–5], and most kinetic studies were focused on dimethyl ether burning characteristics [6–10].

The decomposition reaction starts with the unimolecular initiation step:



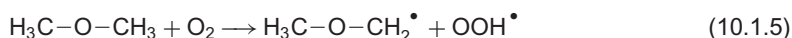
The kinetics of this reaction (for the interval  $790\text{--}950^{\circ}\text{C}$ ) was found to follow the Arrhenius equation [1]:

$$k = 2.16 \times 10^{15} \exp\left(-\frac{76600}{RT}\right) \text{ s}^{-1} \quad (10.1.4)$$

The free radicals generation from reaction 10.1.3 is followed by various propagation and termination reactions. Some of these reactions are shown in Table 10.1.1.

At the temperatures where dimethyl ether decomposition takes place, HCHO is also decomposed easily into  $\text{H}_2$  and CO (see Section 15.1).

In the presence of oxygen, besides the formation of  $\text{CH}_3^{\bullet}$  and  $\text{CH}_3\text{O}^{\bullet}$  radicals, other free radicals are formed, particularly some generated as a result of interactions with  $\text{HOO}^{\bullet}$  and  $\text{OH}^{\bullet}$  radicals. The formation of  $\text{HOO}^{\bullet}$  radical may result directly from the reaction of oxygen with dimethyl ether:



In one study, 78 molecular and radical species and 336 chemical reactions were used to model dimethyl ether oxidative pyrolysis for various ether/oxygen ratios ( $0.2 \leq \phi \leq 2.5$ ) [2]. In a different study performed using shock tube experiments, pyrolysis and oxidative pyrolysis of dimethyl ether diluted with argon was studied in the temperature range  $950\text{--}1900\text{ K}$ , at pressures between 0.8 atm and 2.9 atm. In this study, the pyrolysis process was modeled using 53 species and 178 reactions, including submechanisms of pyrolysis/oxidation for formaldehyde, acetylene, and ethylene [11]. The inhibition of the pyrolysis process of dimethyl ether by NO and by  $\text{C}_3\text{H}_6$  has also been reported [12].

The next homolog of dimethyl ether is ethyl methyl ether,  $\text{CH}_3\text{CH}_2\text{--O--CH}_3$ . The compound has very similar properties with dimethyl ether, including a high CN. In addition, ethyl methyl ether has a b.p. =  $7.7^{\circ}\text{C}$ , which is higher than that of dimethyl ether and makes the compound a better candidate as a diesel fuel. Pyrolysis and oxidative pyrolysis of the compound have been studied using shock tube experiments applying an array of techniques for product analysis [13]. The experiments were conducted on various gas mixtures including ethyl methyl ether diluted with argon (98% and 99.6% Ar), and ethyl methyl ether in the presence of oxygen (ether/oxygen ratio  $0.11 < \phi < 0.44$ ) also diluted with argon. The compounds identified in the pyrolysates included  $\text{H}_2$ , CO,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{CH}_3\text{CHO}$ , and at low levels propyne ( $\text{C}_3\text{H}_4$ ), allene ( $\text{C}_3\text{H}_4$ ),  $\text{C}_3\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , and 1,3-butadiene. The reaction products  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,

TABLE 10.1.1. Propagation and termination reactions during dimethyl ether pyrolysis

Reaction
$\text{CH}_3\text{OCH}_3 + \text{CH}_3^{\bullet} \rightarrow \text{CH}_4 + \text{CH}_3\text{OCH}_2^{\bullet}$
$\text{CH}_3\text{OCH}_2^{\bullet} \rightarrow \text{HCHO} + \text{CH}_3^{\bullet}$
$\text{CH}_3\text{OCH}_2^{\bullet} \rightarrow \text{CH}_4 + \text{CHO}^{\bullet}$
$\text{CHO}^{\bullet} \rightarrow \text{CO} + \text{H}^{\bullet}$
$\text{CH}_3\text{O}^{\bullet} \rightarrow \text{HCHO} + \text{H}^{\bullet}$
$\text{CH}_3\text{O}^{\bullet} \rightarrow \text{HCO}^{\bullet} + \text{H}_2$
$\text{CH}_3\text{OCH}_3 + \text{H}^{\bullet} \rightarrow \text{H}_2 + \text{CH}_3\text{OCH}_2^{\bullet}$
$\text{CH}_3^{\bullet} + \text{H}^{\bullet} \rightarrow \text{CH}_4$
$\text{HCO}^{\bullet} + \text{H}^{\bullet} \rightarrow \text{HCHO}$
$\text{HCO}^{\bullet} + \text{CH}_3^{\bullet} \rightarrow \text{CH}_4 + \text{CO}$

CH<sub>3</sub>CHO, H<sub>2</sub>, and CO were the expected result of an aliphatic ether pyrolysis (CO and H<sub>2</sub> generated from HCHO). The other compounds were mainly by-products of secondary reactions. The study covered a temperature range between 900 K and 1750 K. Most reactions were found to have a first order kinetics and follow Arrhenius equation  $k = A \exp(-E^\ddagger/RT)$ . The values for the frequency factor *A* (per second), activation energy  $E^\ddagger$  (cal/mol), and heats of reaction  $\Delta H^\circ$  (cal/mol) for the main reactions involved in ethyl methyl ether pyrolysis are given in Table 10.1.2.

In the presence of oxygen, in addition to the reactions shown in Table 10.1.2, some other ones involving OH<sup>•</sup> and O<sup>••</sup> radicals take place. These reactions also follow a simple Arrhenius equation, and the values for *A* (per second) and  $E^\ddagger$  (cal/mol) as well as the heats of reaction  $\Delta H^\circ$  (cal/mol) are given in Table 10.1.3.

Based on the analytical data generated in the experiments and using 219 reactions that involve 59 molecular and radicalic species, it was possible to model very precisely both pyrolysis and oxidative pyrolysis of ethyl methyl ether [13].

Pyrolysis of diethyl ether starts between 500 °C and 550 °C. The main reaction taking place at these temperatures is the formation of acetaldehyde and ethane, as shown below:

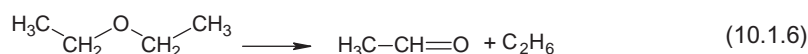


TABLE 10.1.2. The values for the frequency factor *A* (per second) and activation energy  $E^\ddagger$  (cal/mol) in Arrhenius equation and for the heats of reaction (cal/mol) for the main reactions involved in ethyl methyl ether pyrolysis [13]

No.	Reaction	<i>A</i> (s <sup>-1</sup> )	$E^\ddagger$ (cal/mol)	$\Delta H^\circ$ (cal/mol)
1	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> → CH <sub>3</sub> <sup>•</sup> + CH <sub>3</sub> CH <sub>2</sub> O <sup>•</sup>	2.5 × 10 <sup>15</sup>	81000	81000
2	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> → CH <sub>3</sub> O <sup>•</sup> + CH <sub>3</sub> CH <sub>2</sub> <sup>•</sup>	2.0 × 10 <sup>15</sup>	82000	82000
3	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> → CH <sub>3</sub> <sup>•</sup> + CH <sub>3</sub> OCH <sub>2</sub> <sup>•</sup>	2.5 × 10 <sup>15</sup>	82000	82000
4	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> + H <sup>•</sup> → C <sub>2</sub> H <sub>5</sub> OCH <sub>2</sub> <sup>•</sup> + H <sub>2</sub>	1.5 × 10 <sup>14</sup>	8000	-11000
5	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> + H <sup>•</sup> → CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> <sup>•</sup> + H <sub>2</sub>	1.0 × 10 <sup>14</sup>	7000	-12000
6	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> + H <sup>•</sup> → CH <sub>3</sub> OCH <sup>•</sup> CH <sub>3</sub> + H <sub>2</sub>	7.0 × 10 <sup>13</sup>	6000	-13000
7	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> + CH <sub>3</sub> <sup>•</sup> → CH <sub>4</sub> + C <sub>2</sub> H <sub>5</sub> OCH <sub>2</sub> <sup>•</sup>	3.0 × 10 <sup>12</sup>	10000	-11000
8	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> + CH <sub>3</sub> <sup>•</sup> → CH <sub>4</sub> + CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> <sup>•</sup>	3.0 × 10 <sup>12</sup>	9000	-12000
9	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> + CH <sub>3</sub> <sup>•</sup> → CH <sub>4</sub> + CH <sub>3</sub> OCH <sup>•</sup> CH <sub>3</sub>	2.0 × 10 <sup>12</sup>	8000	-13000
10	CH <sub>3</sub> CH <sub>2</sub> O <sup>•</sup> → CH <sub>3</sub> <sup>•</sup> + HCHO	1.8 × 10 <sup>12</sup>	17000	10000
11	CH <sub>3</sub> CH <sub>2</sub> O <sup>•</sup> → H <sup>•</sup> + CH <sub>3</sub> CHO	2.4 × 10 <sup>13</sup>	17000	15000
12	CH <sub>3</sub> OCH <sub>2</sub> <sup>•</sup> → CH <sub>3</sub> <sup>•</sup> + HCHO	1.0 × 10 <sup>14</sup>	33000	8000
13	C <sub>2</sub> H <sub>5</sub> OCH <sub>2</sub> <sup>•</sup> → C <sub>2</sub> H <sub>5</sub> <sup>•</sup> + HCHO	1.8 × 10 <sup>12</sup>	17000	9000
14	CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> <sup>•</sup> → CH <sub>3</sub> O <sup>•</sup> + C <sub>2</sub> H <sub>4</sub>	1.0 × 10 <sup>12</sup>	34000	26000
15	CH <sub>3</sub> OCH <sup>•</sup> CH <sub>3</sub> → CH <sub>3</sub> <sup>•</sup> + CH <sub>3</sub> CHO	2.0 × 10 <sup>12</sup>	30000	6000
16	CH <sub>3</sub> OCH <sup>•</sup> CH <sub>3</sub> → CH <sub>3</sub> O <sup>•</sup> + C <sub>2</sub> H <sub>4</sub>	1.0 × 10 <sup>12</sup>	34000	27000

TABLE 10.1.3. The values for *A* (per second),  $E^\ddagger$  (cal/mol), and  $\Delta H^\circ$  (cal/mol) for the main reactions in ethyl methyl ether pyrolysis in the presence of oxygen [13]

No.	Reaction	<i>A</i>	$E^\ddagger$ (cal/mol)	$\Delta H^\circ$ (cal/mol)
1	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> + OH <sup>•</sup> → C <sub>2</sub> H <sub>5</sub> OCH <sub>2</sub> <sup>•</sup> + H <sub>2</sub> O	4.5 × 10 <sup>13</sup>	4000	-26000
2	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> + OH <sup>•</sup> → CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> <sup>•</sup> + H <sub>2</sub> O	5.0 × 10 <sup>13</sup>	4000	-27000
3	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> + OH <sup>•</sup> → CH <sub>3</sub> OCH <sup>•</sup> CH <sub>3</sub> + H <sub>2</sub> O	5.0 × 10 <sup>13</sup>	4000	-28000
4	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> + O <sup>••</sup> → C <sub>2</sub> H <sub>5</sub> OCH <sub>2</sub> <sup>•</sup> + OH <sup>•</sup>	4.5 × 10 <sup>13</sup>	5000	-9000
5	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> + O <sup>••</sup> → CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> <sup>•</sup> + OH <sup>•</sup>	5.0 × 10 <sup>13</sup>	5000	-10000
6	CH <sub>3</sub> OC <sub>2</sub> H <sub>5</sub> + O <sup>••</sup> → CH <sub>3</sub> OCH <sup>•</sup> CH <sub>3</sub> + OH <sup>•</sup>	5.0 × 10 <sup>13</sup>	5000	-11000

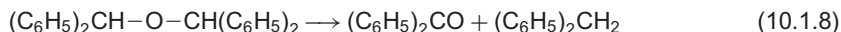
In the same range of temperatures where the ether decomposes, acetaldehyde also undergoes thermal decomposition to generate  $\text{CH}_4$  and  $\text{CO}$ . As the temperature increases above  $600^\circ\text{C}$ , the main pyrolysis products of diethyl ether are  $\text{H}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_3\text{-CHO}$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_4$ . Various studies regarding the kinetic aspects of diethyl ether pyrolysis are published in the literature [14,15].

### Other aliphatic ethers

As seen for the first three aliphatic ethers previously discussed, in order to have an aldehyde generated as a result of thermal decomposition, both carbons connected to the oxygen atoms must contain hydrogens. For the case of other ethers with the oxygen connected to a primary carbon, the reaction takes place similarly, as shown below for dibenzyl ether:



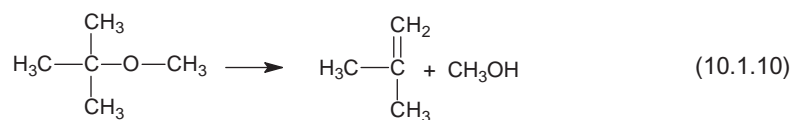
For ethers with the oxygen connected to two secondary carbons, typical pyrolysis products are a hydrocarbon and a ketone, as shown below for (diphenylmethoxy)diphenylmethane, which generates benzophenone and diphenylmethane at around  $300^\circ\text{C}$ :



For ethers with a tertiary carbon bonded at one side of the oxygen and a primary or secondary carbon on the other, thermal decomposition may follow the general rule to generate a hydrocarbon and an aldehyde or a ketone, or may produce a different result, depending on the strengths of the other bonds in the molecule. As an example, triphenyl methyl ether decomposes above  $300^\circ\text{C}$  following reaction 10.1.1 as shown below:



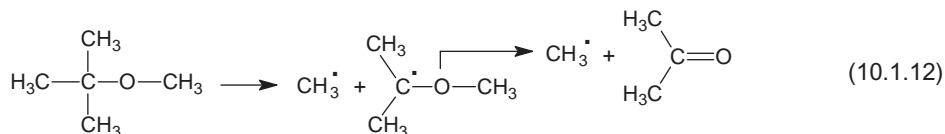
On the other hand, pyrolysis of methyl *tert*-butyl ether takes place by two main mechanisms, one involving a molecular elimination and the other the formation of free radicals by the cleavage of a C-C bond. Molecular elimination seems to represent the predominant mechanism starting around  $575^\circ\text{C}$ , and the reaction is shown below:



The reaction rate for this reaction depends on temperature following Arrhenius equation:

$$k = 7.94 \times 10^{13} \exp\left(\frac{-247(\text{kJ})}{RT}\right) \text{ s}^{-1} \quad (10.1.11)$$

The radicalic mechanism with the cleavage of the 2,3 C-C bond becomes important above  $875^\circ\text{C}$ , and the reaction is shown below:



Reaction 10.1.10 generates, unexpectedly, methanol and an unsaturated hydrocarbon. In reaction 10.1.12, a ketone and a hydrocarbon ( $\text{CH}_4$ ) are generated, but the expected result from the general rule of decomposition would be different.

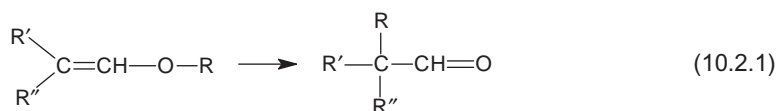


The interest in pyrolysis of methyl *tert*-butyl ether and its higher homologs was driven by the fact that these compounds were used as fuel additives with the role of antiknocking agents. These oxygenated compounds improve the completeness of fuel burning and reduce hydrocarbon emissions in internal combustion engines. Pyrolysis of methyl *tert*-butyl ether labeled with deuterium at the methyl group bonded to the oxygen atom showed that in reaction 10.1.10, labeled methanol is generated, and in reaction 10.1.12, the acetone does not contain deuterium. Similar decomposition with methyl *tert*-butyl ether was verified for 2-methoxy-2-methylbutane, 2-methoxy-2,3-dimethylbutane, 2-methoxy-2,3,3-trimethylbutane, and 2-methoxy-2,4,4-trimethylpentane [16]. In these compounds, the methanol is eliminated up to 850 °C, and 2,3-C–C bond cleavage occurs above 875 °C. For these compounds, it was also verified that the 1,2-C–C bond cleavage is not a likely reaction in the range from 875 °C to 950 °C.

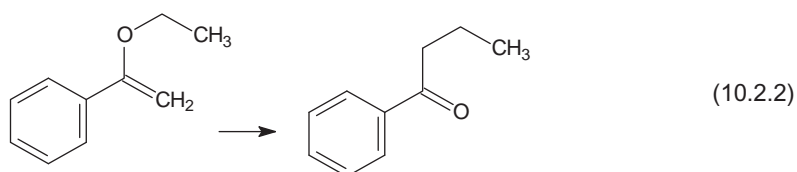
## 10.2. UNSATURATED ETHERS

### General aspects

Different from enols, which are not stable compounds, unsaturated ethers have a higher thermal stability. For example, both ethyl vinyl ether and divinyl ether (vinyl ether) are stable compounds at room temperature. Due to their reactivity, these compounds are used in organic synthesis. Vinyl ether was used as an anesthetic. At temperatures around 300 °C, a typical reaction for the unsaturated ethers is the isomerization to form aldehydes or ketones as shown in reaction below:



For example, 1-ethoxy-1-phenyl ethene generates by mild pyrolysis around 300 °C 1-phenylbutan-1-one:



In pyrolysis of unsaturated ethers, it is possible that traces of water play a role in the reaction outcome since these compounds are easily hydrolyzed.

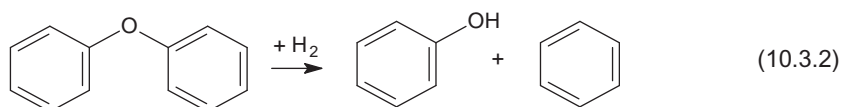
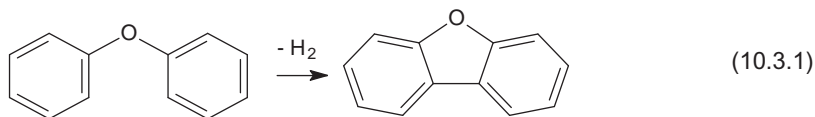
## 10.3. AROMATIC ETHERS

### General aspects

Ethers with both substituents at the oxygen atom consisting of aromatic rings are used or have been used in many practical applications. Diphenyl ether (biphenyl ether, phenoxybenzene) has been used as a cooling fluid. A number of derivatives of diphenyl ether are used as pesticides, and brominated phenoxybenzenes were widely used as flame retardants, particularly in flexible polyurethane foams and in the polymers used for printed electronic circuit boards. The use of diphenyl ether herbicides can lead to the accumulation of these compounds in plants and soil. Burning of plant material treated with diphenyl ether herbicides may lead to the generation of halogenated dibenzofurans and dioxins. The flame retardants also can be subject to pyrolysis, particularly in industrial incinerators that process large amounts of plastics.

**Diphenyl ether and diphenyl ether type herbicides**

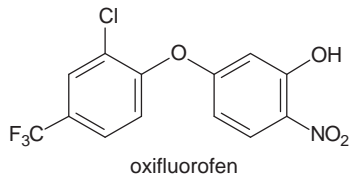
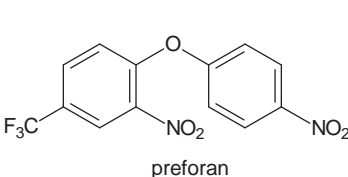
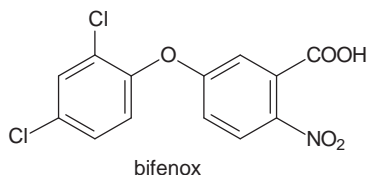
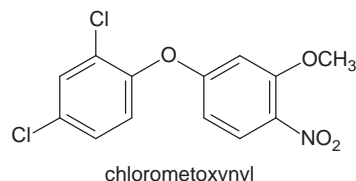
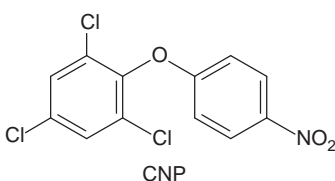
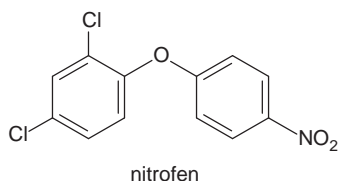
Diphenyl ether has a high thermal stability and does not decompose at temperatures around 450 °C. At temperatures around 800 °C, the decomposition occurs with the formation of dibenzofuran, benzene, and phenol. The overall reactions accounting for this result can be written as follows:



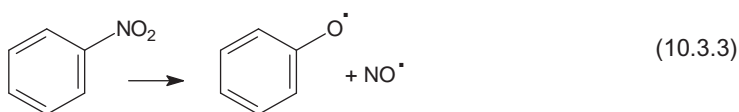
The mechanism for reaction 10.3.1 is very likely radicalic. It is possible that the free  $\text{H}^\bullet$  radicals generated in the initiation step interact in a propagation process with diphenyl ether molecules and lead to reactions of the type 10.3.2. It is also possible that the molecular hydrogen formed in reaction 10.3.1 interacts with the ether to form phenol and benzene.

The formation of dibenzodifuran by thermal decomposition of diphenyl ether is not a desired process from an environmental and health prospective. The compound is listed as a pollutant of concern due to its persistence in the environment, but it is not classifiable as a human carcinogen. However, in the presence of molecular halogens or halogen free radicals, “de novo” chlorinated or brominated dibenzofurans, which are of greater concern, can be generated.

A few pesticide derivatives of diphenyl ether are shown below:

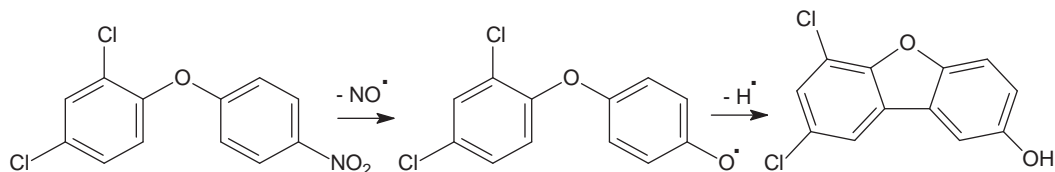


Pyrolysis of diphenyl ether pesticides is not reported in the literature. The substituent group from these molecules, which is likely to be the first to decompose as the temperature increases, is the nitro group. The compounds with an aromatic nitro group may decompose involving the following reaction [17] (see Section 14.1):



Applying similar mechanism for the nitro substituted diphenyl ethers, the first stage in pyrolysis would be the formation of phenoxy type radicals. The free radicals generated in this manner can easily lead to

the formation of dibenzofurans as shown below for nitrofen:

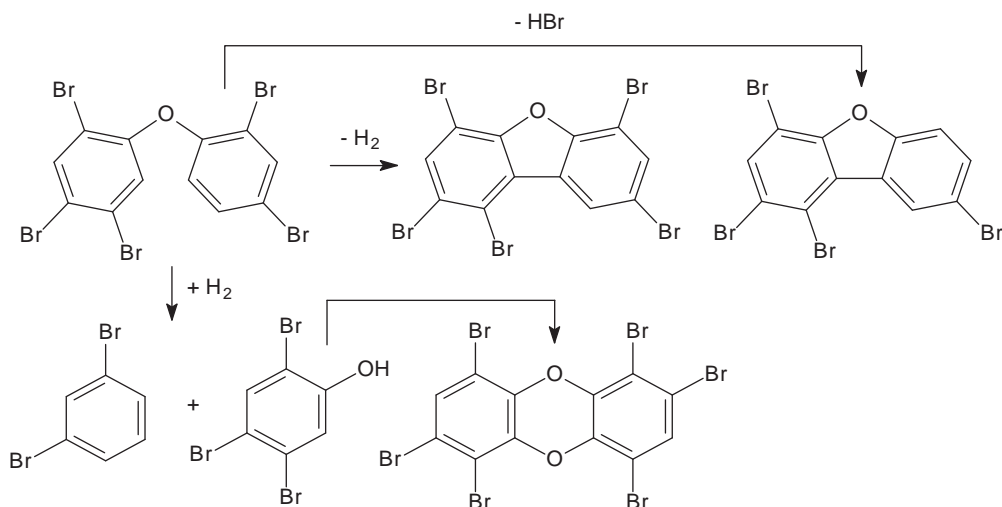


A compound such as preforan would have a high propensity to form dibenzodioxins.

### Polybrominated diphenyl ethers

The (poly)brominated diphenyl ethers, also known as PBDE, can have 209 congeners, known under various acronyms. For example, bis(pentabromophenyl) ether or decabromodiphenyl oxide has as acronyms DBDE, decaBDE, etc. and pentabromodiphenyl ether has as acronyms pentaBDE, PeBDE, PBDE, PBDO, etc. A congener number is sometimes used for indicating a specific compound (e.g., 2,2',4,4',5-pentabromodiphenyl ether is known as PBDE-99). Commercial products are commonly a mixture of various congeners, and a pentaBDE, may contain tetra, penta, and hexabromodiphenyl ethers. Many PBDEs were used in mixtures. Considerable effort has been invested in the evaluation of formation of halogenated dibenzodioxins and dibenzofurans from flame-retardant brominated diphenyl ethers. Studies were done to determine the formation of these undesirable compounds when the flame retardants were subject to thermolysis, pyrolysis/gasification, and various types of combustion conditions [18–20].

Pyrolysis of polybrominated diphenyl ethers is a source of brominated dibenzofurans (furans) and brominated dibenzodioxins (dioxins). Similar to reaction 10.3.1, the brominated compounds generate directly brominated dibenzofurans. A reaction of the type 10.3.2 forms brominated phenols, which form both brominated furans and brominated dioxins as shown in Section 9.5. These types of reactions are indicated schematically below:



The elimination of  $\text{Br}^\bullet$ , which further forms either  $\text{Br}_2$  or  $\text{HBr}$ , is also typical for these compounds. The  $\text{Br}^\bullet$  free radicals and  $\text{HBr}$  play an important role in the fire retardation process. However, both  $\text{HBr}$  and  $\text{Br}_2$  are sources for “de novo” generation of brominated dibenzofurans and brominated dibenzodioxins. At high temperatures and in the presence of organic or inorganic sources of chlorine (e.g., polyvinyl

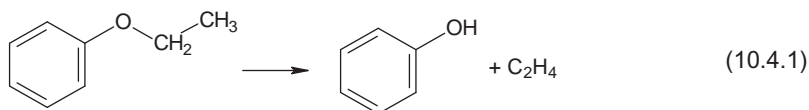
chloride), an exchange of bromine-substituted furans and dioxins has been noticed [21]. The end result is a mixture of chlorinated and brominated furans and dioxins.

The formation of brominated furans and dioxins evaluated during thermal processing of plastics indicated that even in relatively mild conditions, these compounds are formed from the brominated flame retardants [22]. The largest levels of brominated furans and dioxins were found as generated during accidental and uncontrolled fires. These fires are characterized by insufficient oxygen and pyrolysis at temperatures between 650 °C and 850 °C and are able to generate considerable amounts of brominated furans and dioxins from the flame retardants. Pyrolysis at very high temperatures and controlled combustion as practiced in industrial incinerators, with temperatures above 850 °C, residence time higher than 2 s, and excess of oxygen, may lead to efficient destruction of the undesirable compounds since the halogenated dibenzofurans and dibenzodioxins also decompose at these temperatures [23].

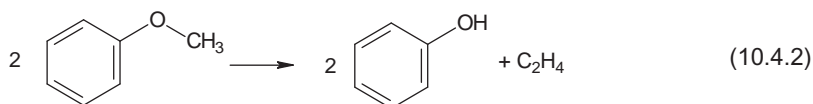
#### 10.4. ETHERS WITH ONE ALKYL AND ONE ARYL SUBSTITUENT

##### General aspects

Mixed substituents to the oxygen are common in many ethers. This category contains numerous natural compounds with strong olfactory characteristics (anisole, alkyl anisols, anethole, estragol, etc). Other ethers such as benzyl phenyl ether are present in bituminous coals. The common thermal decomposition reaction for this type of ethers leads to the formation of a phenol and a hydrocarbon, as shown below for ethyl phenyl ether (ethoxybenzene or phenetole):

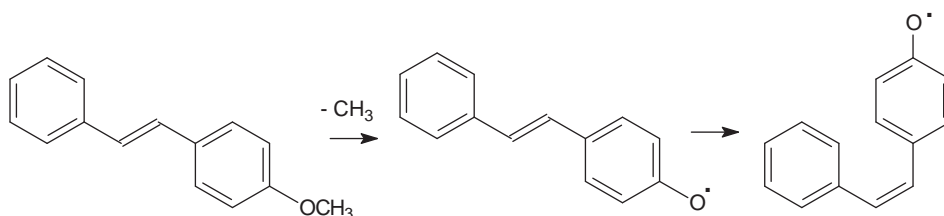


At temperatures between 380 °C and 400 °C, anisole (methyl phenyl ether) also generates phenol and ethylene. The reaction can be written as follows:

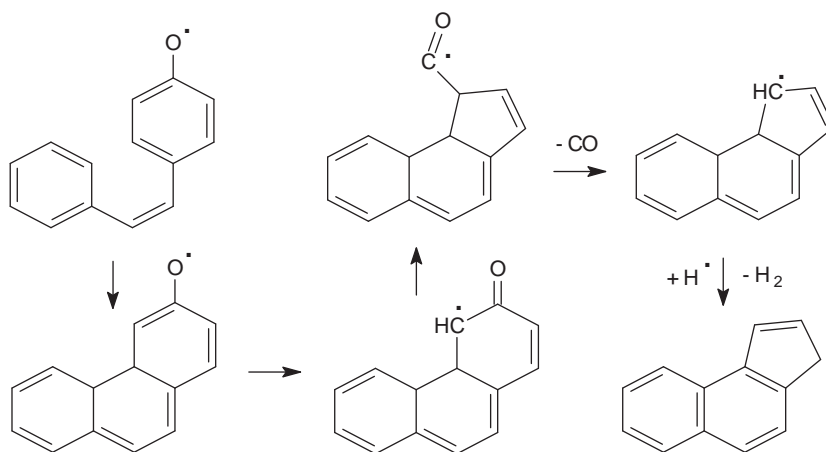


Similar reactions were followed around 350 °C by  $\beta$ -naphthyl ethyl ether and around 400 °C by isobutyl phenyl ether and 2-ethoxy-4-methyl-1-(methylethyl)benzene. Benzyl phenyl ether pyrolyzed around 375 °C generated phenol, toluene, and higher molecular weight compounds including char. Pyrolysis in the presence of hydrogen sources increases the content of phenol and benzene [24].

Pyrolysis of ethers usually takes place with a radicalic mechanism. Following the formation of the free radicals, and depending on the structure of the molecule, various rearrangements can take place. For example, pyrolysis of 1-(2-phenylvinyl)-4-methoxybenzene starts with an initiation reaction as shown below:

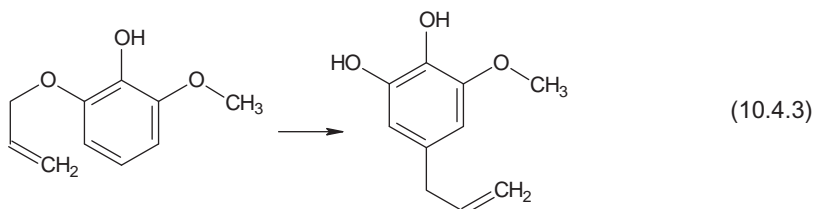


The free radicals generated in this reaction, following an electrocyclization, further form a tricyclic compound as shown below [25]:

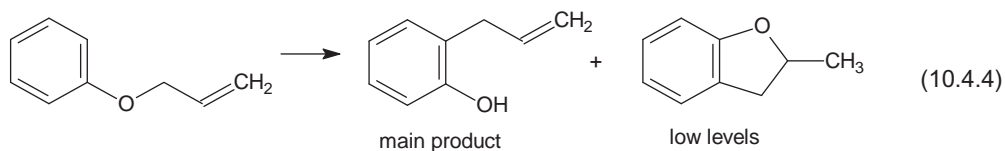


Various areno[*e*]indenes can be formed by similar reactions [25]. The benzene ring substituted to the methoxystyryl can be replaced with thiophene, benzothiophene, or benzofuran.

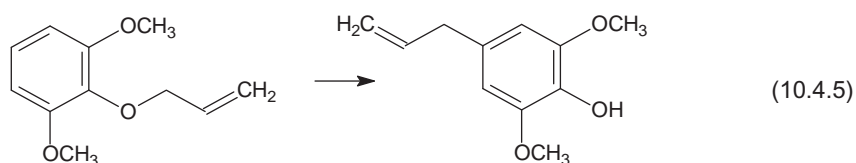
Another type of rearrangement during pyrolysis is known to occur for phenyl propenyl ethers. Due to the relatively good stability of the allyl radicals, the allyl group can migrate from the bond with the oxygen atom to the aromatic ring. One example is shown below for 6-methoxy-2-propenyl-1-oxyphenol, which generates by heating 3-methoxy-5-propenyl-catechol [26]:



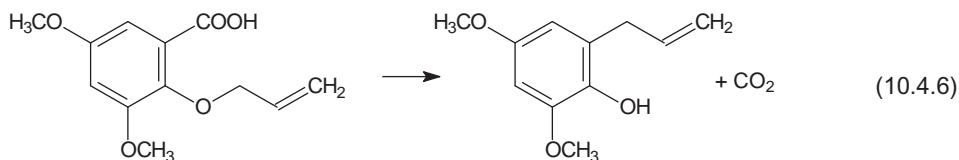
The reaction is rather general, and the presence of the OH group or of methoxy group in 6-methoxy-2-propenyl-1-oxyphenol is not required for the reaction to take place. Propenyl phenyl ether heated around 280 °C undergoes the following reaction:



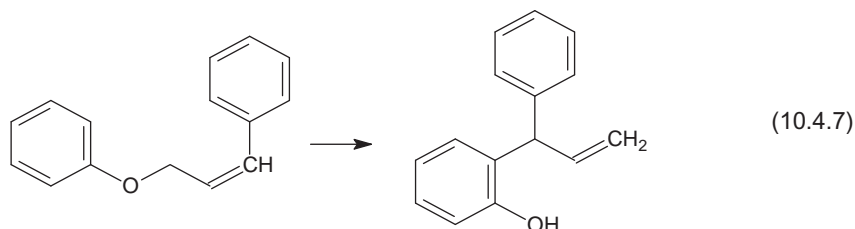
As seen in reaction 10.4.4, the allyl group migrates into the *ortho*-position of the benzene ring. If the *ortho*-positions are blocked, the migration takes place into *para*-position as shown in the reaction below:



Some groups such as CHO or COOH in *ortho* are even removed by pyrolysis from the benzene ring of allyl phenyl ethers if the other *ortho* and the *para* positions are not available on the benzene ring, as shown in the example below:

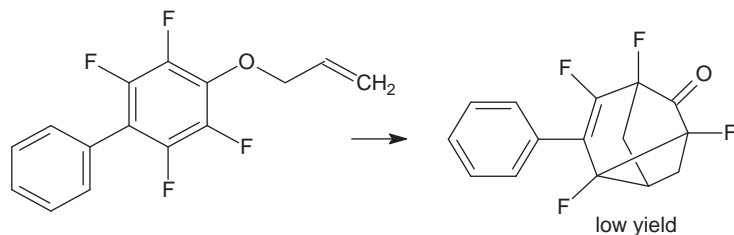


Pyrolysis of phenyl cinnamyl ether reveals an interesting aspect of this rearrangement during the pyrolysis of allyl phenyl ethers. The reaction for phenyl cinnamyl ether takes place as follows:



This reaction (and similar ones) indicates that the  $\gamma$ -carbon of the allyl group is the one that becomes attached to the benzene ring, followed by the rearrangement of the double bonds.

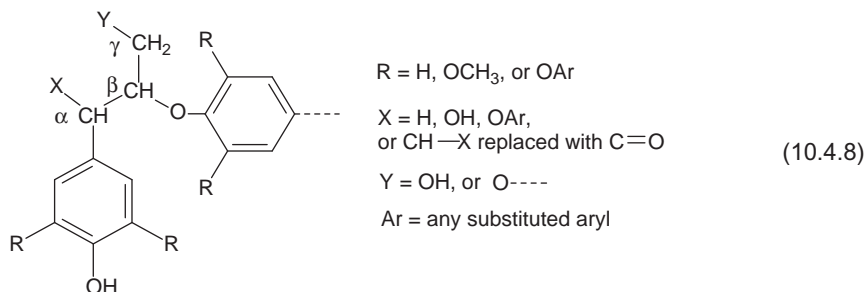
For the allyl ethers where all the positions in the phenoxy ring are occupied, the reaction may occur with intramolecular Diels–Alder rearrangements as reported for flash vapor phase pyrolysis at 350 °C of 2,3,5,6-tetrafluoro-4-phenyl-1-prop-2-enyloxybenzene, which generates among other compounds 2,4,5,7-tetrafluoro-3-phenyltricyclo[3.3.1.0<sup>2,7</sup>]non-3-ene-6-one, as shown below [27]:



1-Propenyl naphthyl ether generates 2-propenyl-1-naphthol, in a manner similar to the reactions for propenyl phenyl ethers. Propargyl phenyl ethers do not follow reactions similar to their allyl homolog.

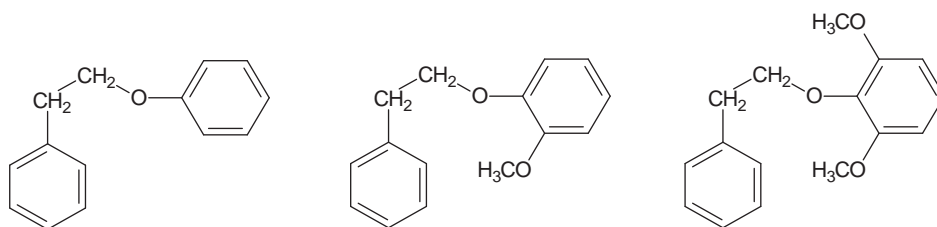
### Model ethers for lignin structure

Lignin makes up about 15–36% of wood (at dry weight). For this reason, lignin is subject to numerous studies, some involving pyrolysis (see, e.g., [28]). Lignin's polymeric structure does not have a unique repeating unit. However, substituted phenylpropanes connected by ether bonds are the basic units for lignin. A simplified structure for lignin is shown below:



Depending on the nature of the R in the phenylpropane unit, three types of ideal lignins are recognized. The 4-hydroxyphenylpropane unit is indicated as H, the 4-hydroxy-3-methoxyphenylpropane or guaiacylpropane unit is indicated as G, and 4-hydroxy-3,5-dimethoxyphenylpropane or syringylpropane unit is indicated as S. Based on the occurrence of the basic units, lignins can be classified as G lignins or guaiacyl lignins (also known as type N) when the G groups are dominant, G/S lignins or guaiacyl-syringyl lignins (also known as type L), and H/G/S lignins. The three atoms in the propane chain are labeled as  $\alpha$ ,  $\beta$ , and  $\gamma$ , and at least one is further connected through ether bonds. Particularly, the  $\beta$ C is always connected to a phenoxy group (or a substituted phenoxy O–Ar where the aryl Ar can be further connected in the lignin molecule).

The mechanism of cleavage by heat of the ether linkages in lignin has been studied on model compounds such as (2-phenylethoxy)benzene, 2-methoxy-1-(2-phenylethoxy)benzene, and 1,3-dimethoxy-2-(2-phenylethoxy)benzene [29]. The structures of these model compounds are shown below:



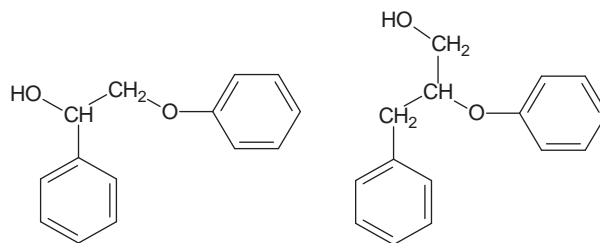
The main pyrolysis products at 500 °C in a flash vacuum pyrolysis experiment [29] for these compounds are shown in Table 10.4.1.

Another set of model compounds used for the understanding of lignin pyrolysis included 1-phenyl-2-phenoxyethanol and 3-phenyl-2-phenoxypropan-1-ol [30]. The structures of these model compounds

TABLE 10.4.1. The main pyrolysis products generated from (2-phenylethoxy)benzene, 2-methoxy-1-(2-phenylethoxy)benzene, and 1,3-dimethoxy-2-(2-phenylethoxy)benzene at 500 °C in a flash vacuum pyrolysis experiment [29]

No.	Compound	(2-Phenylethoxy)-benzene	2-Methoxy-1-(2-phenylethoxy)-benzene	1,3-Dimethoxy-2-(2-phenylethoxy)-benzene
1	Phenol	55.9 ± 2.8%	7.5 ± 1.0%	
2	Styrene	40.5 ± 2.5%	19.7 ± 0.7%	16.3 ± 1.3%
3	Ethylbenzene	0.38 ± 0.07%	2.9 ± 0.2%	3.3 ± 0.1%
4	2-Phenylethylbenzene	1.5 ± 0.1%	0.77 ± 0.04	0.56 ± 0.01%
5	Toluene	0.25 ± 0.05%	0.56 ± 0.15%	0.31 ± 0.02%
6	Benzaldehyde	1.4 ± 0.3%		
7	2-Hydroxybenzaldehyde		32.4 ± 3.1%	
8	2-Methoxyphenol		18.2 ± 1.7%	2.3 ± 0.1%
9	Catechol		8.8 ± 0.5	
10	6-Methoxy-(2-phenylethyl)phenol		5.0 ± 2.2%	
11	1-Methoxybenzaldehyde		1.6 ± 0.3%	
12	2-Methylphenol (o-cresol)			24.0 ± 0.3%
13	2,6-Dimethoxyphenol			12.8 ± 0.6%
14	2-Hydroxy-3-methoxybenzaldehyde			9.4 ± 0.6
15	2-Hydroxy-3-methylbenzaldehyde			7.6 ± 0.4%
16	6-Hydroxy-2-methoxybenzaldehyde			5.3 ± 0.2%

are shown below:



The main pyrolysis products at 500 °C for these compounds are shown in Table 10.4.2.

Pyrolysis of compounds such as derivatives of cinnamyl alcohol [31], lignin dimers [32,33], and lignin trimers [34,35] were reported. A theoretical approach for the pyrolysis of phenetyl phenyl ether can also be found in the literature [36]. Depending on various substituents on the carbons in the propane chain, various reaction mechanisms are followed. For example, for the dimer 1-(4-hydroxy-3-methoxyphenyl)-2-phenoxypropane-1-hydroxy-3-X (X = H or OH), the reaction may proceed through the formation of a quinone methide (for X = OH) or through a radical chain reaction involving a  $\beta$ -ether cleavage (for X = H) as shown below:

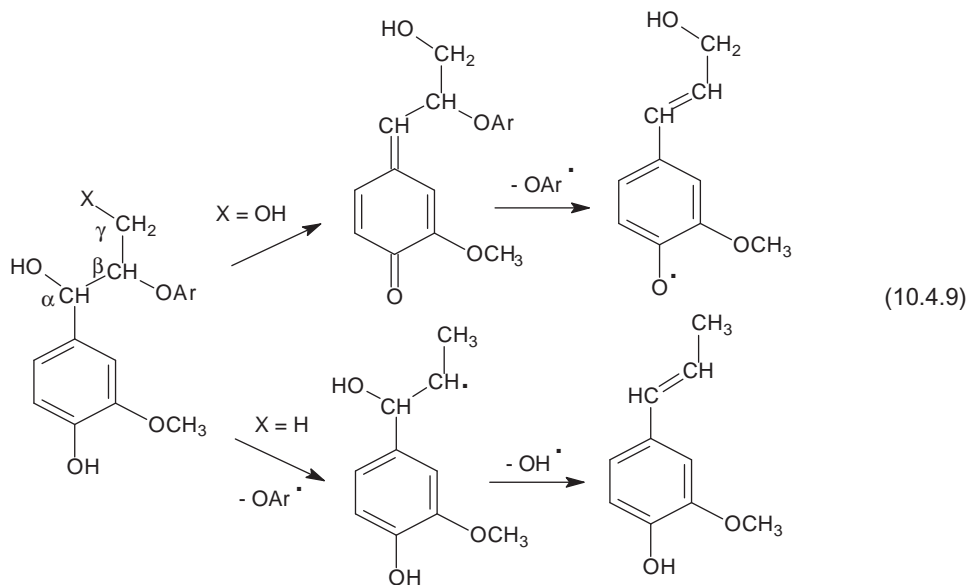


TABLE 10.4.2. The main pyrolysis products generated from 1-phenyl-2-phenoxyethanol and 3-phenyl-2-phenoxypropan-1-ol at 500 °C in a flash vacuum pyrolysis experiment [30]

No.	Compound	1-Phenyl-2-phenoxyethanol	3-Phenyl-2-phenoxypropan-1-ol
1	Phenol	30.6 ± 0.8%	48.4 ± 0.2%
2	Styrene	1.1 ± 0.1%	1.7 ± 0.1%
3	Benzaldehyde	1.9 ± 0.3%	
4	2-Phenylethanal	33.3 ± 0.7%	
5	Acetophenone	3.1 ± 0.1%	
6	(2-Phenylvinyl)oxybenzene	32.5 ± 1.8%	
7	3-Phenyl-2-propen-1-ol		3.6 ± 0.1%
8	2-Propenylbenzene		3.2 ± 0.2%
9	3-Phenylpropanal		34.9 ± 0.5%
10	Indene		8.1 ± 0.5%



Some other idealized structures for lignin were also proposed [37]. Lignin can be seen, for example, as a polymer of coniferyl alcohol (4-hydroxy-3-methoxycinnamyl alcohol). Pyrolysis of coniferyl alcohol (mainly *trans* isomer) leads to the pyrogram shown in Figure 10.4.1. The pyrolysis was performed with 0.60 mg compound, in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and a housing temperature of  $T_{\text{hou}} = 280^\circ\text{C}$ . The analysis of the pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications in the pyrogram and their relative molar content in 100 moles of pyrolysate are given in Table 10.4.3. The calculation of the mole percent was obtained based solely on peak areas, and since differences in the MS response factors can be quite large for different compounds, the estimations may have large errors.

Some coniferyl alcohol remains undecomposed, although equal quantities of *cis* and *trans* isomers are retrieved in the pyrolysate when the initial material is mainly *trans*. (see Section 2.4). The main pyrolysis products include a variety of compounds such as carbon dioxide, formaldehyde, 2,4-dimethylphenol, 2-methoxy-4-vinylphenol, 4-propenylphenol, 4-methyl-1,2-benzenediol, 2-methoxy-4-(1-propenyl)phenol, 2-methyl-6-(2-propenyl)phenol, 4-hydroxy-3-methoxybenzaldehyde (vanillin), 2-methoxy-4-propylphenol, 4-hydroxy-3-methoxybenzeneacetic acid (homovanillic acid), and 4-hydroxy-2-methoxycinnamaldehyde. This result shows the complexity of reactions occurring during pyrolysis. Formation of formaldehyde and 2-methoxy-4-vinylphenol indicates the cleavage of 3-hydroxy-1-propenyl group; the presence of methyl on the benzene ring indicates migration of the  $\text{CH}_3$  group in a reaction similar to 10.4.2; formation of vanillin and homovanillic acid and that of 2-methoxy-4-(1-propenyl)-phenol shows the presence of oxidation–reduction processes. Related to lignin are numerous natural small molecules, such as the catechins. Catechins are phenolic compounds also containing an ether group. The more common catechins include catechin and epicatechin (which are epimers), epigallocatechin, etc. These compounds are present, for example, in tea leaves and in cocoa. Pyrolysis of these compounds generates mainly di- and trihydroxybenzenes [38].

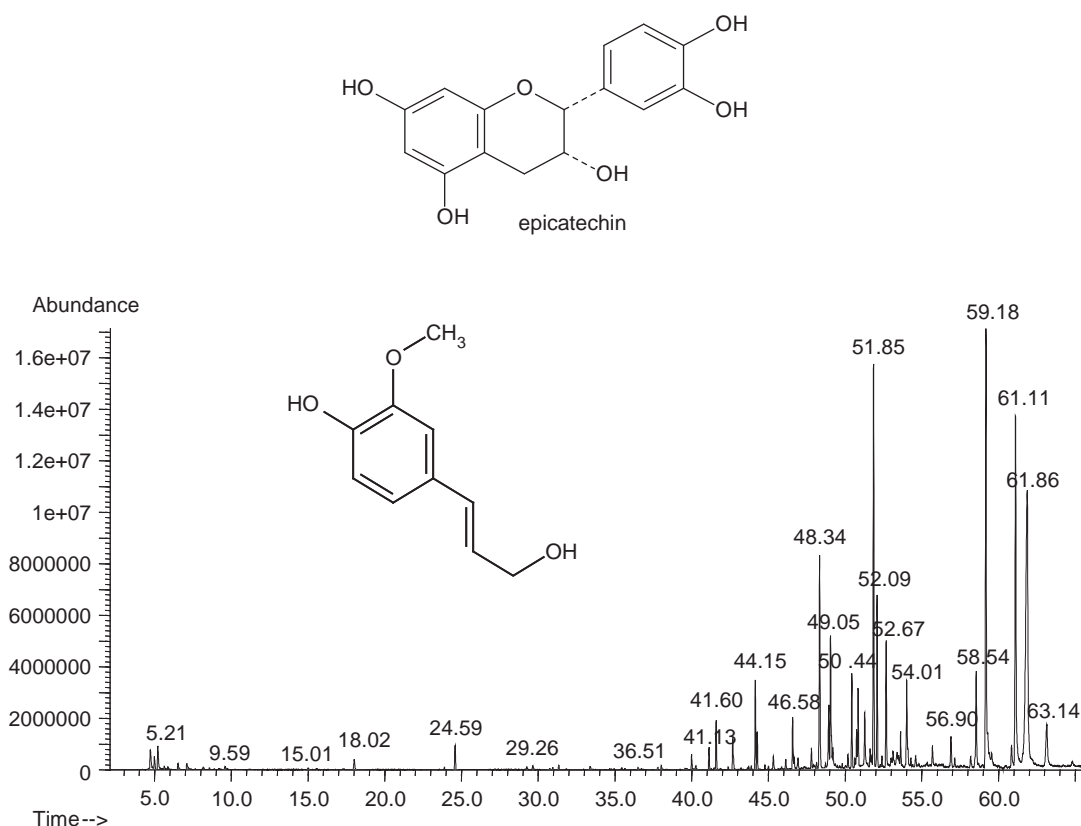


FIGURE 10.4.1. Pyrogram of (mainly *trans*)-4-(3-hydroxy-1-propenyl)-2-methoxyphenol (coniferyl alcohol) generated at  $900^\circ\text{C}$ .

TABLE 10.4.3. Identification of the main peaks in the chromatogram shown in Figure 10.4.1 for the pyrolysis of 4-(3-hydroxy-1-propenyl)-2-methoxyphenol (*trans*-coniferyl alcohol) (hydrogen, CO, methane, ethane, and water are not included)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Propene	4.88	42	115-07-1	7.17
2	Carbon dioxide	4.72	44	124-38-9	2.46
3	1-Propene	4.98	42	115-07-1	1.25
4	Formaldehyde	5.21	30	50-00-0	2.98
5	Acetaldehyde	6.52	44	75-07-0	0.57
6	Methanol	7.10	32	67-56-1	0.93
7	1,3-Pentadiene	8.16	68	2004-70-8	0.11
8	Furan	8.57	68	110-00-9	0.07
9	1,3-Cyclopentadiene	9.59	66	542-92-7	0.19
10	3-Methylenecyclopentene	15.01	80	N/A	0.09
11	1,3-Cyclohexadiene	15.57	80	592-57-4	0.06
12	4-Methylenecyclopentene	15.01	80	14548-32-4	0.06
13	Benzene	18.02	78	71-43-2	0.59
14	Toluene	24.59	92	108-88-3	0.91
15	Ethylbenzene	29.26	106	100-41-4	0.08
16	1,3-Dimethylbenzene ( <i>m</i> -xylene)	29.66	106	108-38-3	0.14
17	1,4-Dimethylbenzene ( <i>p</i> -xylene)	30.96	106	106-42-3	0.05
18	Styrene	31.34	104	100-42-5	0.06
19	2-Cyclopenten-1-one	31.84	82	930-30-3	0.07
20	Benzofuran	36.51	118	271-89-6	0.05
21	2-Methyl-2-cyclopenten-1-one	37.78	96	1120-73-6	0.02
22	1H-Indene	38.03	116	95-13-6	0.11
23	Phenol	40.00	94	108-95-2	0.51
24	7-Methylbenzofuran	40.27	132	17057-52-8	0.13
25	2-Methoxyphenol	41.13	124	90-05-1	0.56
26	2-Methylphenol	41.60	108	95-48-7	1.44
27	2,6-Dimethylphenol	42.38	122	576-26-1	0.06
28	4-Methylphenol	42.68	108	106-44-5	1.15
29	2,4-Dimethylphenol	44.15	122	105-67-9	2.38
30	2-Methoxy-4-methylphenol	44.27	138	93-51-6	0.87
31	4-Ethylphenol	45.33	122	123-07-9	0.41
32	3-Ethyl-5-methylphenol	46.13	136	698-71-5	0.23
33	2-Ethyl-4-methylphenol	46.59	136	3855-26-3	1.13
34	1,4-Dimethoxy-2-methylbenzene	46.68	152	24599-58-4	0.27
35	2-Methyl-5-hydroxybenzofurane	46.93	148	6769-56-8	0.28
36	Unknown	47.81	120	N/A	0.52
37	2,2,-Bifuran	48.14	134	5905-00-0	0.15
38	2-Methoxy-4-vinylphenol	48.34	150	7786-61-0	4.97
39	2-Methyl-1-naphthol	48.75	158	7469-77-4	0.04
40	2-Methoxy-4-(2-propenyl)phenol	48.94	164	97-53-0	1.42
41	4-Propenylphenol	49.05	134	1745-81-9	3.78
42	1-Methoxy-4-(1-propenyl)benzene	49.09	148	104-46-1	0.04
43	1,2-Benzenediol	49.20	110	120-80-9	0.65

TABLE 10.4.3. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
44	1,2-Dimethoxy-4-(1-propenyl)benzene	50.19	178	93-16-3	0.20
45	2-Methoxy-4-(1-propenyl)phenol	50.44	164	97-54-1	1.84
46	2-Methyl-1,4-benzenedicarboxaldehyde	50.65	148	27587-17-3	0.25
47	3-Isopropylbenzaldehyde	50.75	148	34246-57-6	0.86
48	2-(2-methyl-2-propenyl)phenol	50.85	148	20944-88-1	1.74
49	4-Methyl-1,2-benzenediol	51.28	124	452-86-8	2.02
50	7-Methylbenzofuran	51.63	132	17059-52-8	0.50
51	1H-Indenol	51.72	132	56631-57-3	0.30
52	2-Methoxy-4-(1-propenyl)phenol	51.85	164	1076-55-7	8.27
53	2-Methyl-6-(2-propenyl)phenol	52.09	148	3354-58-3	3.70
54	2-( <i>o</i> -Anisyl)-1-butene	52.40	162	N/A	0.20
55	4-Hydroxy-3-methoxybenzaldehyde (vanillin)	52.68	152	121-33-5	2.99
56	4-Ethylcatechol	53.48	138	1124-39-6	0.37
57	<i>p</i> -(1-Ethylvinyl)anisole	53.62	162	21758-19-0	0.59
58	2-Methoxy-4-propylphenol	54.01	166	2785-87-7	2.00
59	2-Methoxy-4-methyl-6-propenylphenol	54.09	178	201359-63-9	0.32
60	4-(3-Methyl-2-butenyl)phenol?	54.29	162	1200-09-5	0.19
61	1-(4-Hydroxy-3-methoxyphenyl)ethanone	54.60	166	498-02-2	0.13
62	2-Methyl-6-propylphenol	54.60	150	3520-52-3	0.16
63	4-Hydroxy-2-methylbenzaldehyde	55.69	135	41438-18-0	0.56
64	4-Methoxybenzenepropanol	58.18	166	5406-18-8	0.30
65	4-Hydroxy-3-methoxybenzeneacetic acid (homovanillic acid)	58.54	182	306-08-1	2.26
66	4-((1E)-3-Hydroxy-1-propenyl-2-methoxy)phenol (coniferyl alcohol)	59.18	180	458-35-5	9.79
67	Unknown	59.54	164	N/A	0.47
68	Unknown	60.84	178	N/A	0.60
69	4-((1Z)-3-Hydroxy-1-propenyl-2-methoxy)phenol (coniferyl alcohol)	61.11	180	N/A	9.67
70	4-Hydroxy-2-methoxycinnamaldehyde	61.86	178	127321-19-1	15.96
71	5-Hydroxy-3-methyl-1-indanone	63.14	162	57878-30-5	1.90

## 10.5. EPOXIDES AND LARGER CYCLIC ETHERS

### General aspects

Cyclic ethers can be considered (nonaromatic) heterocyclic compounds. The ethers with three atoms in the ring are indicated as oxiranes, with four as oxetanes, with five as tetrahydrofurans, and with six as tetrahydropyrans. Oxiranes are also known as epoxides. The epoxy group can be regarded as a functional group, and larger molecules including it are named using the prefix epoxy associated with the name of the longest carbon chain (counting the two carbon atoms from the ring). Epoxyethane (ethylene oxide) is the simplest oxirane. Due to the fact that bond angles for each atom deviate significantly from

the optimum values, epoxides have a highly strained ring and are more reactive than other ethers. Epoxides are used as intermediates in organic synthesis and for the production of certain polymers. Oxetanes (or trimethyleneoxides) also have highly strained cycles. The five- and six-membered cyclic ethers do not have strained rings and have properties similar to those of acyclic ethers.

### Ethylene oxide and other oxiranes

Ethylene oxide starts decomposing around 550 °C to generate methane and CO as the main reaction products, and also ethane, ethylene, acetylene, acetaldehyde, propane, and hydrogen. The decrease in the mole percent of the parent compound as a function of temperature for 1 s pyrolysis time is shown in Figure 10.5.1.

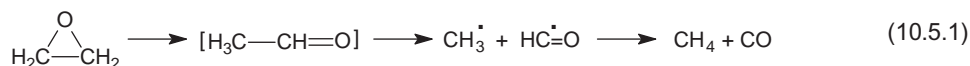
The total rate constant of reaction for the temperature range 830–1200 K obtained from a shock tube experiment [39] is described by the Arrhenius equation:

$$k = 1.21 \times 10^{14} \exp \left[ \frac{-57.2(\text{kcal/mol})}{RT} \right] \text{ s}^{-1}$$

Another study using shock tube pyrolysis performed in the temperature range 1200–1800 K with pressures from 0.19 atm to 0.40 atm [40] leads to the following expression for Arrhenius equation:

$$k = 2.6 \times 10^{13} \exp \left[ \frac{-58.6(\text{kcal/mol})}{RT} \right] \text{ s}^{-1}$$

The thermal decomposition main mechanism involves free radicals and can be written as follows [41]:



The reaction starts with the cleavage of a C–O bond to form the biradical  $^\bullet\text{CH}_2\text{CH}_2\text{O}^\bullet$  (triplet state) followed by a 1,2-H shift to form  $\text{CH}_3\text{CH}=\text{O}$ . It is likely that the molecule of acetaldehyde is in an excited state having about 7 kcal in excess compared to C–C dissociation energy for acetaldehyde [42]. For this reason, most acetaldehyde is decomposed by a unimolecular mechanism, generating two free radicals. The presence of these free radicals explains the formation of the minor decomposition products. Also, the interaction of  $\text{CH}_3^\bullet$  free radicals with ethylene oxide (and an H transfer) can

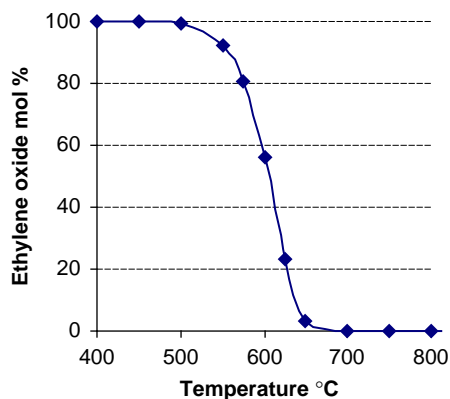
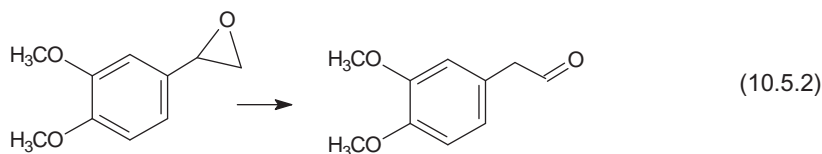


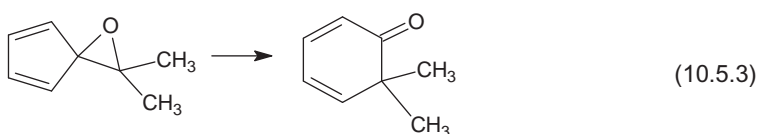
FIGURE 10.5.1. The decrease in the mole percent of ethylene oxide with temperature (1 s pyrolysis time).

generate oxiranyl free radicals, which also participate in the propagation of the reaction [43]. Part of the acetaldehyde present in excited state can lose energy by molecular collisions, which explains the presence of low levels of acetaldehyde in the pyrolysate.

Similar to ethylene oxide, pyrolysis of other oxiranes leads to the formation of aldehydes. For example, 1,2-dimethoxyphenyl-4-oxiran-2-ylbenzene generates 2-(3,4-dimethoxyphenyl)ethanal [44]:

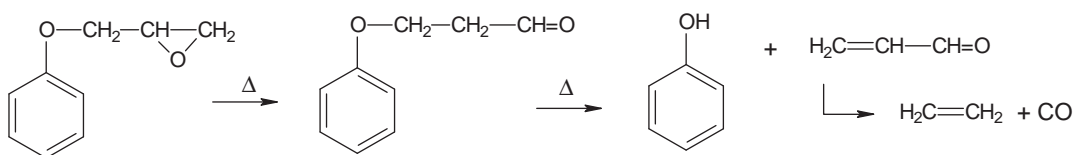


Pyrolysis of other oxiranes typically leads to the opening of the three-atom ring with the formation of a carbonyl compound. In spirooxiranes, the opening of the three-atom ring may be associated with the expansion of the adjacent ring [45], as shown in the following reaction:



These types of reactions were utilized for various pyrolytic syntheses.

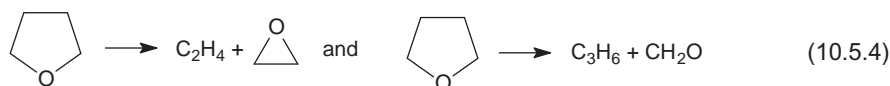
Among epoxides that are also ethers and have applications in polymer industry are diglycidyl ether or oxiran-2-yl(oxiran-2-ylmethoxy)methane, phenyl glycidyl ether, and diglycidyl resorcinol ether or 1,3-bis(oxiran-2-ylmethoxy)benzene. The thermal decomposition of these compounds is related to the thermal decomposition of various polymers generated using these compounds [46]. The pyrolysis process starts with the opening of the oxirane ring and the formation of the isomeric aldehydes, followed by the cleavage of the ether bond when the heating continues or the thermal decomposition takes place at higher temperatures. The main reactions in the pyrolysis of phenyl glycidyl ether are shown below:



The other two compounds undergo similar reactions during pyrolysis.

### 1,4-Tetrahydrofuran, 1,4-dioxane, and related compounds

Thermal decomposition of tetrahydrofuran leads to a mixture of compounds including  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ , ethylene oxide, and formaldehyde. It was suggested that the decomposition is initiated by parallel reactions involving the ring cleavage [47] as shown below:



Pyrolysis of tetrahydrofuran has also been studied in the presence of nickelocene for the generation of carbon nanotubes [48].

Pyrolysis of dioxane in a static reactor at 510 and 550 °C at pressures below 19 Torr and reaction times from 1 min to 10 min leads to conversion rates between 1% and 25% [49]. The pyrolysis generates

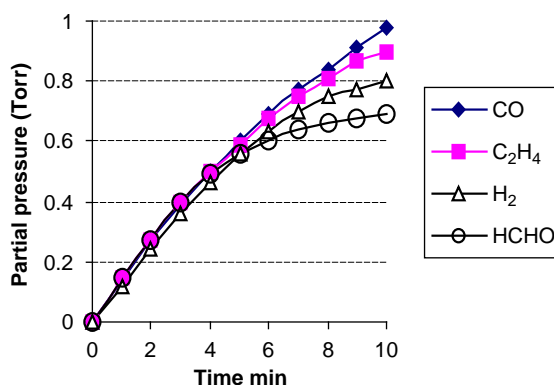


FIGURE 10.5.2. Partial pressure of the main pyrolysis products of dioxane as a function of heating time at 510 °C and initial pressure of 14.25 Torr [49].

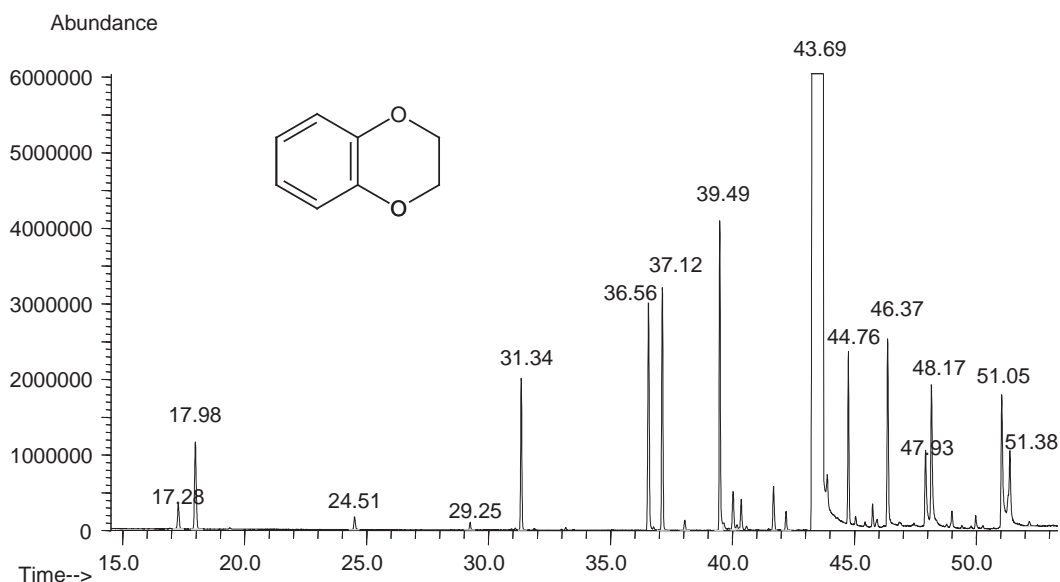


FIGURE 10.5.3. Pyrogram of 1,4-benzodioxan at 900 °C.

CO, H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and HCHO as the main reaction products and several minor products including C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>-CHO, CH<sub>4</sub>, CH<sub>2</sub>=CH-CHO, and CH<sub>3</sub>-CH=CH<sub>2</sub>. The variation in partial pressure of the main pyrolysis products as a function of heating time at 510 °C and initial pressure of 14.25 Torr is shown in Figure 10.5.2.

The pyrolysis mechanism involves the formation of free radicals, as proven by the addition of NO (a free radical inhibitor), which slows down the reaction. Comparing the bond dissociation energies for C-H (93 kcal/mol), C-O (85 kcal/mol in diethyl ether), and C-C (79 kcal/mol in methyl propyl ether), it can be concluded that the most likely initiation reaction takes place with the cleavage of the C-C bond. Thermal decomposition of 1,4-dioxane follows the reaction steps shown below:

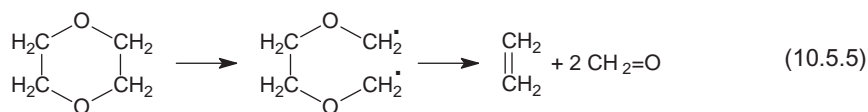
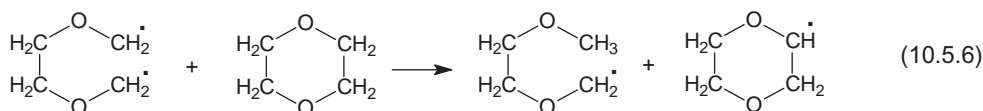


TABLE 10.5.1. Identification of the main peaks in the chromatogram shown in Figure 10.5.3 for the pyrolysis of 1,4-benzodioxan (ethene and water not measured)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	1,3-Butadiene	5.91	54	106-99-0	1.27
2	1,3-Cyclohexadiene	17.28	80	592-57-4	2.17
3	Benzene	17.98	78	71-43-2	8.23
4	Toluene	24.51	92	108-88-3	0.85
5	Ethylbenzene	29.25	106	100-41-4	0.40
6	Styrene	31.34	104	100-42-5	7.77
7	Benzaldehyde	36.56	106	100-52-7	12.71
8	1-(2-hydroxyphenyl)ethanone	37.13	136	118-93-4	9.52
9	Indene	38.06	116	95-13-6	0.50
10	Impurity (tributylamine)	39.49	185	102-82-9	Not included
11	2,2'-Bifuran	39.65	134	5905-00-0	0.47
12	Phenol	40.04	94	108-95-2	2.63
13	Benzyl alcohol	40.19	108	100-51-6	0.36
14	Unknown	40.37	132	N/A	1.40
15	2-Methylphenol	41.70	108	95-48-7	2.42
16	3-Methyl-1H-indene	42.21	130	767-60-2	0.79
17	2,3-Dihydro-1,4-benzodioxin (benzodioxan)	43.69	136	493-09-4	Not included
18	Naphthalene	43.90	128	91-20-3	9.53
19	Impurity (2-chloroethoxybenzene)	44.76	156	622-86-6	Not included
20	3(2H)-benzofuranone	45.45	134	7169-34-8	0.42
21	Cinnamaldehyde (E)	46.38	132	14371-10-9	8.67
22	Cinnamaldehyde (Z)	47.93	132	104-55-2	4.60
23	2,3-Dihydro-1H-inden-1-one	48.17	132	83-33-0	9.00
24	Biphenyl	49.01	154	92-52-4	0.86
25	2-Methylbenzofuran	51.05	132	4265-25-2	8.06
26	1H-Indenol	51.38	132	56631-57-3	7.06
27	Biphenylene	52.18	152	259-79-0	0.32

The formaldehyde formed in reaction 10.5.5 can decompose further with the formation of CO and H<sub>2</sub>. These reactions account for the main pyrolysis products of dioxane. Other propagation reactions are also possible, generating a variety of free radicals as shown below:



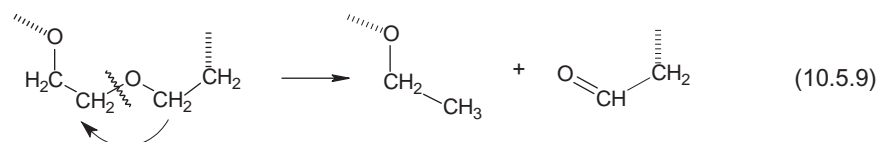
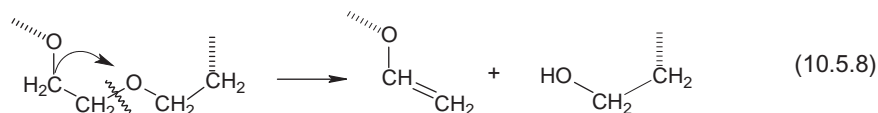
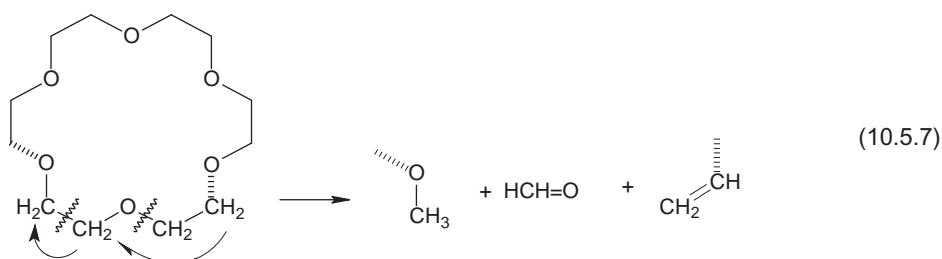
The formation of these free radicals explains the formation of the minor pyrolysis products of dioxane.

Thermal decomposition of 1,4-benzodioxan generates a mixture of compounds as shown in the pyrogram of Figure 10.5.3. The pyrolysis was performed with 0.60 mg compound, in Type 1 Experiment as described in Section 4.6,  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and a housing temperature of  $T_{\text{hou}} = 280^\circ\text{C}$ . The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications in the pyrogram and their relative molar content in 100 moles of pyrolysate (excluding 1,4-benzodioxan) are given in Table 10.5.1. The calculation of the mole percent was obtained based solely on peak areas.

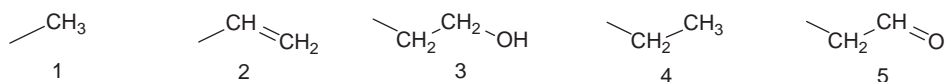
As shown in Figure 10.5.3, 1,4-benzodioxan is the major peak in the pyrogram. However, this does not indicate a high stability of the parent molecule to heating, since the experiment was performed in conditions that allowed part of the material to vaporize before reaching the pyrolysis temperature. The cleavage of both C–O and C–C bonds is obvious from the list of pyrolysis products that include 1-(2-hydroxyphenyl)ethanone, naphthalene, cinnamaldehyde, etc. The presence of benzaldehyde and other compounds indicates that various rearrangements take place during pyrolysis. Dioxolane and 1,3-benzodioxol are expected to show similar pyrolysis behavior as 1,4-dioxane and benzodioxane, respectively.

### Crown ethers

Pyrolysis of crown ethers takes place with the cleavage of C–O or C–C bonds. This can be exemplified by performing the pyrolysis of 18-crown-6 ether. The results obtained from 0.5 mg material in a Type 1 Experiment as described in Section 4.6 at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and a housing temperature of  $T_{\text{hou}} = 280^\circ\text{C}$  indicated that the molecular fragments in the pyrolysate are the result of the following type of reactions (see also [50]):



The fragmentation takes place at one or more points along the ring. Some of the fragmentations can occur as the first stage of pyrolysis, but subsequent fragmentations of the molecules generated in a first pyrolysis step are also likely. When the pyrolysate was analyzed by GC/MS under conditions given in Table 4.6.1, the main pyrolysis products were formaldehyde and acetaldehyde (hydrogen, water, methane, and ethylene were not measured due to the setting of the mass range  $m/z \geq 29$  for the mass spectral detection). Lower levels of oxirane, cyclopropane, 1,4-dioxane, ethanol, and 3-methyl-1,3-dioxolane were also detected. Tentatively identified (by mass spectra only) were propanal and butanal. The other molecular fragments detected in the pyrolysates resulting from reactions 10.5.7 to 10.5.9 had the following terminal moieties:


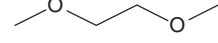

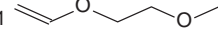

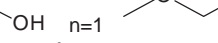

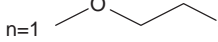

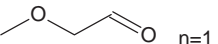

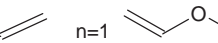

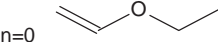

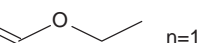


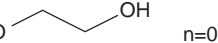

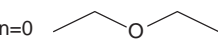

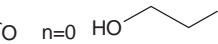



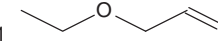

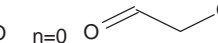


Some of the compounds in the pyrolysate included these terminal moieties connected to a hydrogen to generate  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{C}_2\text{H}_6$ , and  $\text{CH}_3\text{CHO}$ . Other pyrolysate components included the same moieties connected either with an –O– atom or with – $\text{CH}_2\text{--CH}_2\text{--O--}$  (MW = 44) groups. A few examples of molecules detected in the 18-crown-6 ether are shown in Table 10.5.2.

Pyrolysis results for other crown ethers were reported in the literature [51] showing mechanisms similar to that of 18-crown-6 ether.



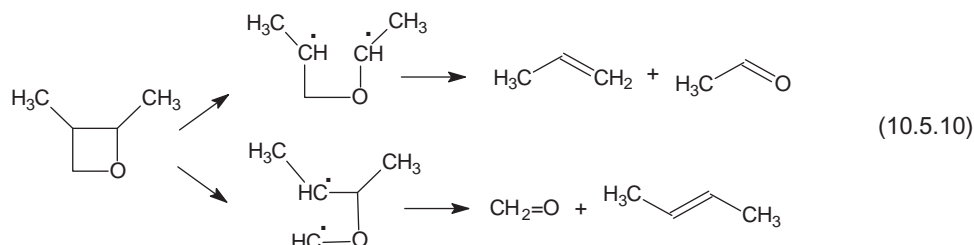
TABLE 10.5.2. Fragment molecules generated from the cleavage of 18-crown-6 ether

Combination of terminal moieties	MW*	Examples
1+1	$46+n \times 44$	$n=0$  , $n=1$ 
1+2	$58+n \times 44$	$n=0$  , $n=1$ 
1+3	$76+n \times 44$	$n=0$  , $n=1$ 
1+4	$60+n \times 44$	$n=0$  , $n=1$ 
1+5	$74+n \times 44$	$n=-1$ $\text{HCH=O}$ , $n=0$  , $n=1$ 
2+2	$70+n \times 44$	$n=0$  , $n=1$ 
2+3	$88+n \times 44$	$n=-1$  , $n=0$ 
2+4	$72+n \times 44$	$n=-1$ $\text{C}_2\text{H}_4$ , $n=0$  , $n=1$ 
2+5	$86+n \times 44$	$n=1$ 
3+3	$106+n \times 44$	$n=-2$ $\text{H}_2\text{O}$ , $n=-1$  , $n=0$ 
3+4	$90+n \times 44$	$n=-1$  , $n=0$ 
3+5	$104+n \times 44$	$n=-1$  , $n=0$ 
4+4	$74+n \times 44$	$n=0$  , $n=1$ 
4+5	$88+n \times 44$	$n=-1$  , $n=1$ 
5+5	$102+n \times 44$	$n=-1$  , $n=0$ 

\* $n$  can take negative or positive integer values and indicates the number of  $-\text{CH}_2-\text{CH}_2-\text{O}$  groups intercalated in the molecule.

### Other cyclic ethers

Pyrolysis of oxetanes typically takes place by a radicalic mechanism with the cleavage of a C—C bond, generating an alkene and a carbonyl compound as shown below for 2,3-dimethyloxetane [52]:

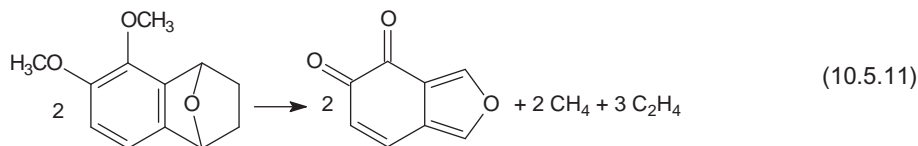


Some other cyclic compounds containing the C—O—C moiety in their molecule are saturated derivatives of aromatic heterocyclic compounds. Examples of these types of molecules include perhydropyran, chromane, and xanthene, which can be considered cyclic ethers.

Pyrolysis of chromane at 413 °C generated *o*-cresol, benzofuran, and styrene in the ratio 4:2:1 as well as C<sub>1</sub> and C<sub>2</sub> hydrocarbon molecules [53]. The pyrolysis study was also performed in the presence of 2-butene and of hydrogen.

Xanthene is very stable to heating, and pyrolysis at 800 °C in flash mode in an analytical pyrolyzer (see Experiment 3 in Section 4.6) leads to practically no decomposition of the sample, only vaporization taking place, and a small proportion of oxidation to xanthen-9-one (xanthone) due to the traces of oxygen present during the pyrolytic process.

Various cyclic ether structures are frequently included in more complex molecules. For example, 3,4-dimethoxy-11-oxatricyclo[6,2,1,0<sup>2,7</sup>]undeca-2(7),3,5-triene contains a moiety similar to that of tetrahydrofuran. This compound generates by pyrolysis isobenzofuran-4,5-dione in a reaction as shown below [54]:

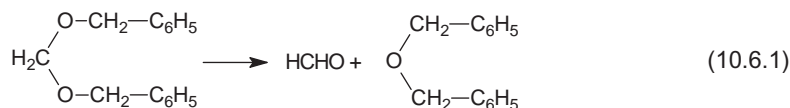


The reaction has been used for the synthesis of dialdehydes by further hydrolysis and rearrangement of the resulting dione.

## 10.6. ACETALS AND HEMIACETALS

### General aspects

Acetals are a special type of ethers. Many of these compounds are hydrolyzed easily, particularly in a basic medium, and their thermal stability is not very high. Upon heating, the acetals typically regenerate the aldehyde and form an ether, as shown in the following reaction for formaldehyde dibenzyl acetal:



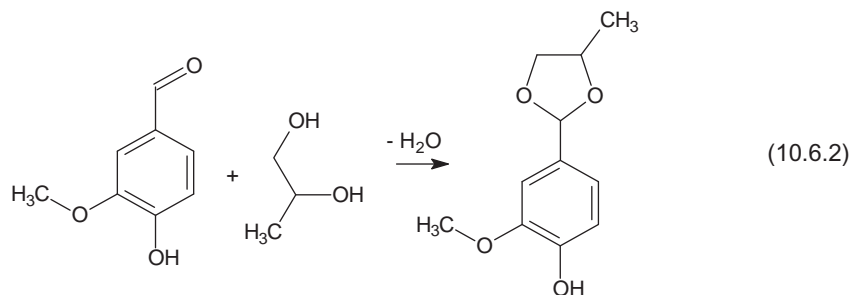
The ether may continue the thermal decomposition if the temperature is high enough.

TABLE 10.6.1. *Pyrolysis results for vanillin propylene glycol acetal at 700 °C for 20 s*

No.	Compound	MW	CAS no.	Relative mole percent
1	1-Propene	42	115-07-1	<b>23.86</b>
2	Acetone	58	67-64-1	7.22
3	Benzene	78	71-43-2	1.06
4	Toluene	92	108-88-3	1.20
5	Benzofuran	118	271-89-6	1.39
6	Propylene glycol	76	57-55-6	<b>12.51</b>
7	3-Methoxybenzaldehyde	136	591-31-1	1.89
8	2-Methoxyphenol	124	90-05-1	1.01
9	2-Methylphenol	108	95-48-7	3.09
10	Phenol	94	108-95-2	2.79
11	2-Ethylphenol	122	90-00-6	1.09
12	Vanillin	152	121-33-5	<b>17.52</b>
13	1,2-Benzenediol (catechol)	110	120-80-9	2.45
14	Vanillin propylene glycol acetal	210	N/A	<b>22.90</b>

Note: The compounds in pyrolysate with a mole percent higher than 10% are in bold.

The acetals of diols, such as propylene glycol (PG), have higher stability than the acetals of monohydroxylic alcohols. For example, vanillin and ethylvanillin form relatively stable acetals with propylene glycol. The reaction is shown as follows for vanillin:



Performed around 250 °C in the presence of moisture, reaction 10.6.2 is reversed, leading to the formation of vanillin and propylene glycol. Pyrolysis at 700 °C of vanillin propylene glycol acetal leads to the formation of numerous fragments indicated in Table 10.6.1.

As shown in Table 10.6.1, even at relatively high temperature, the parent vanillin propylene glycol acetal is still present in the pyrolysate. The stability of this acetal is caused by the stability of the 1,3-dioxolane cycle formed in reaction 10.6.2. Other fragments are formed from the cleavage of a different bond in the acetal molecule.

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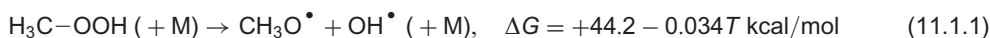
## CHAPTER 11

*Pyrolysis of Peroxy Compounds***11.1. HYDROPEROXIDES*****General aspects***

Organic hydroperoxides are compounds with the formula R–O–OH, where R is an alkyl or aryl organic radical. The R group can also consist of an acyl group. In this case, the resulting compounds are peroxy acids. Peroxy acids (peracids) are discussed in Section 11.4. The O–O bond in hydroperoxide functional group can break easily, generating free radicals. For this reason, hydroperoxides are used as radical initiators in polymerization reactions. Among the most common compounds used for this purpose is methyl ethyl ketone peroxide, CH<sub>3</sub>–C(OOH)<sub>2</sub>–C<sub>2</sub>H<sub>5</sub>. The hydroperoxide of isopropyl benzene (cumene), obtained by the oxidation of isopropyl benzene, is an intermediate compound in an important industrial process for the synthesis of phenol and acetone. Typically, hydroperoxides decompose at low temperatures. For this reason, thermal decomposition of some hydroperoxides is not a true pyrolysis (since the decomposition may take place below 300 °C).

***Methyl hydroperoxide***

The decomposition of methyl hydroperoxide generates free radicals by the reaction:



As suggested in reaction 11.1.1, the process may take place with the participation of an inert molecule M. The reaction has been studied in solution as well as in gas phase [1]. The decomposition in solution (dimethyl phthalate solvent) takes place very rapidly, with a reaction rate (first order) of about  $3 \times 10^{-5} \text{ s}^{-1}$  at 112 °C and  $2 \times 10^{-4} \text{ s}^{-1}$  at 153 °C. Similar to the decomposition of H<sub>2</sub>O<sub>2</sub>, the concentration of M plays a role in reaction kinetics [2]. In gas phase the reaction kinetic was found to be different (and slower). In the presence of toluene vapors, the decomposition of methyl hydroperoxide leads to the formation of dibenzyl, as a result of the reaction of CH<sub>3</sub>O<sup>•</sup> and OH<sup>•</sup> with toluene molecules, and to the formation of benzyl radicals followed by a termination reaction between benzyl radicals. The process was studied in the temperature range 565–650 °C. For a methyl hydroperoxide partial pressure around 25 Torr and a heating time around 0.9 s, the decomposition of methyl hydroperoxide increased from about 16% (at 565 °C) to about 71% (at 651 °C). In gas phase, the Arrhenius equation for methyl hydroperoxide was found to have the expression [1]:

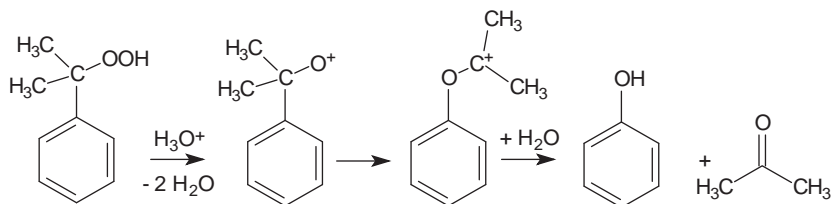
$$k (\text{s}^{-1}) = 10^{11 \pm 2} \exp \left[ \frac{-(32 \pm 5)10^3}{RT} \right] \quad (11.1.2)$$

The molecules formed from methyl hydroperoxide in the presence of an H donor (such as toluene) are CH<sub>3</sub>OH and H<sub>2</sub>O.

***Other hydroperoxides***

Some hydroperoxides are explosive materials, such as methyl ethyl ketone peroxide (2,2-dihydroperoxybutane). Thermal decomposition of this compound has been studied in solution starting

at 32 °C and cannot be considered a pyrolysis [3]. Among the studies of thermal decomposition of hydroperoxides, the decomposition of isopropylbenzene hydroperoxide (2-hydroperoxy-2-phenylpropane, cumene hydroperoxide) received special attention. The compound is industrially prepared by the oxidation of cumene (see, e.g., [4]) and is used to prepare phenol and acetone by hydrolysis in slightly acidic medium. The reaction takes place as follows:



The reactions do not involve the formation of free radicals, but because it is an exothermic process, it may lead to the thermal decomposition of cumene hydroperoxide by a radicalic mechanism and a runaway or explosive reaction. Also, cumene hydroperoxide is used to prepare dicumyl peroxide in a reaction with  $\alpha$ -cumyl alcohol. Dicumyl peroxide is used as an initiator in polymerization reactions. The thermal decomposition of cumene hydroperoxide was studied in cumene solutions at concentrations between 20% and 80%. The reaction order was determined to be 0.5, and Arrhenius parameters were determined to have the values:  $E^a = 122.0 \pm 3.0$  kJ/mol and  $\log A = 20.0 \pm 1.2$  (mol<sup>0.5</sup>/min) [5–7]. The decomposition in other solvents, such as chlorobenzene [4], and the autocatalytic effects during decomposition were also evaluated [8,9]. The main reaction products are  $\alpha$ -cumyl alcohol, acetophenone, di- $\alpha$ -cumyl peroxide, and  $\alpha$ -methylstyrene.

A hydroperoxide used as a free radical initiator or for the synthesis of *tert*-butyl alcohol is *tert*-butyl hydroperoxide. Its thermal decomposition is reported in the literature [10,11].

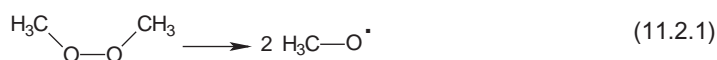
## 11.2. PEROXIDES

### General aspects

Organic peroxides are compounds with the formula R–O–O–R', where R and R' are alkyl or aryl organic radicals. When R (or R') is an acyl group, the compound is a peroxy ester; pyrolysis of these compounds is discussed further in Section 11.4. Similar to the case of hydroperoxides, the O–O bond can break easily, generating free radicals. Peroxides are typically used as radical initiators in polymer industry. Some peroxides are used as explosives such as hexamethylenetriperoxide-diamine (HMTD). Some peroxides are found in nature (e.g., artemisinin). Thermal decomposition of peroxides also takes place at low temperatures, and their thermal decomposition is not truly pyrolysis.

### Dimethyl peroxide

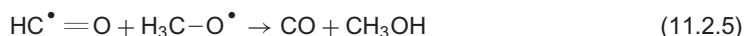
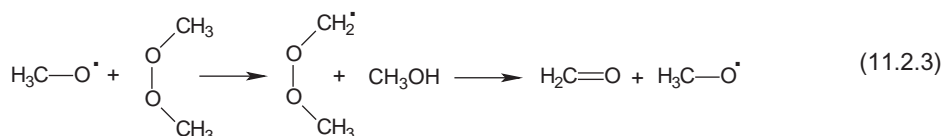
The decomposition of dimethyl peroxide (CH<sub>3</sub>–O–O–CH<sub>3</sub>) has been studied in the range of temperatures 110–140 °C [12] and in a similar range (118–159 °C) [13,14]. The initial decomposition reaction leads to the formation of free radicals by the cleavage of the O–O bond:



The Arrhenius equation for this reaction was reported to have the expression:

$$\log k \text{ (s}^{-1}\text{)} = (15.7 \pm 0.5) - \frac{(37.1 \pm 0.9)}{2.303RT} \quad (11.2.2)$$

Following the initiation reaction with the formation of free radicals, the propagation takes place with the interaction of methoxy radicals with molecules of dimethyl peroxide as shown below:



The end result of this process is the formation of CO and methanol. The overall result can be written as follows:

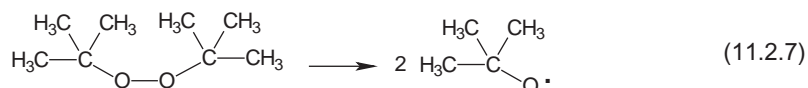


In the range of evaluated temperature, reaction 11.2.6 was found to have a reaction rate  $k \approx 5 \times 10^4 \text{ mol}^{-1} \text{ s}^{-1}$ . The reaction was also studied in the presence of  $\text{NO}_2$  and  $\text{O}_2$  [13].

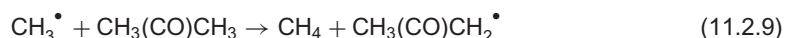
### Other peroxides

Thermal decomposition of several other peroxides is reported in the literature. These include acetone peroxide dimer (3,3,6,6-tetramethyl-1,2,4,5-tetraoxane) and trimer, di-*tert*-butyl peroxide [15–20], dicumyl peroxide [21], di-trifluoromethyl peroxide [22,23], and organosilicon peroxides [24]. Some of these compounds are explosive materials, and their thermal decomposition starts at low temperatures.

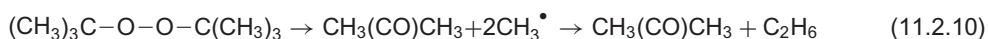
The decomposition of di-*tert*-butyl peroxide in the temperature range 110–180 °C takes place similar to the decomposition of dimethyl peroxide. The initiation reaction occurs as follows:



The formation of free radicals continues with the following propagation reactions:



Termination reactions lead to the formation of ethane, ethyl methyl ketone, and biacetonyl (hexane-2,5-dione). Also, trace amounts of *tert*-butyl alcohol, *tert*-butyl methyl ether, etc., were formed. The main reaction products remain acetone and ethane, with the overall reaction:

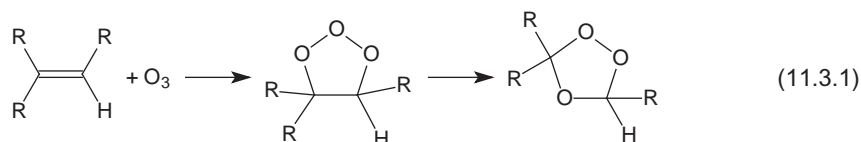


The Arrhenius parameters for this reaction (of first order) were estimated:  $\log A (\text{s}^{-1}) = 15.80 \pm 0.03$  and  $E^a (\text{kJ/mol}) = 158.07 \pm 0.25$  (for the temperature range 90–350 °C) [16]. Another peroxide evaluated regarding its decomposition parameters is 3,3,6,6-tetramethyl-1,2,4,5-tetraoxane (acetone cyclic diperoxide), which decomposes mainly with the formation of acetone [25]. Peroxides with additional functional groups such as peroxyamines are also known, and their thermal decomposition has been reported [26].

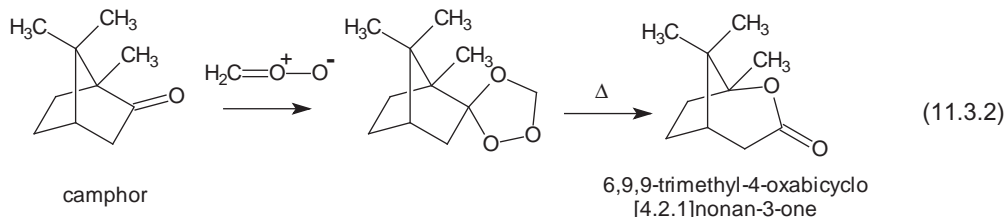
### 11.3. OZONIDES

#### General aspects

Organic ozonides are typically formed in a reaction between ozone and an alkene. The compounds have a trioxolane structure, and their formation can be written as shown below:



Ozonides are not stable compounds, and they decompose at temperatures as low as 70–80 °C. Because the process takes place at low temperatures, the ozonide decomposition was used for synthetic purposes with the preservation of specific structural characteristics of the molecule. One example of such reaction is the preparation of 6,9,9-trimethyl-4-oxabicyclo[4.2.1]nonan-3-one starting with an ozonide generated from camphor and formaldehyde oxide [27]. The reactions are shown below:



Other ozonides decompose thermally with the formation of an unsaturated carboxylic acid [27].

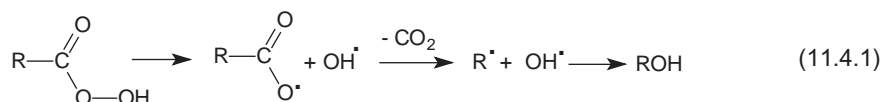
### 11.4. ACYL PEROXIDES

#### General aspects

Several types of compounds contain in their molecule the peroxy group O–O connected to one or two acyl substituents. These groups of compounds include peracids, which have the general formula  $\text{RC}(=\text{O})\text{O}-\text{OH}$ ; peroxy esters, which have the general formula  $\text{R}^1\text{C}(=\text{O})\text{O}-\text{OR}^2$ ; diacyl peroxides with the formula  $\text{R}^1\text{C}(=\text{O})\text{O}-\text{OC}(=\text{O})\text{R}^2$ ; esters of monoperoxydicarboxylic acid with the formula  $\text{R}^1\text{OC}(=\text{O})\text{O}-\text{OR}^2$ ; carbamoyl peroxides with the formula  $\text{R}^1\text{NHC}(=\text{O})\text{O}-\text{OC}(=\text{O})\text{R}^2$ ; peroxy lactones; etc. These compounds can be considered as derivatives of carboxylic acids  $\text{RC}(=\text{O})\text{OH}$ . However, the peroxy group O–O plays the main role in the thermal decomposition of these compounds, and this makes thermal properties of acyl peroxides similar to those of hydroperoxides and peroxides (discussed in Sections 11.1 and 11.2, respectively).

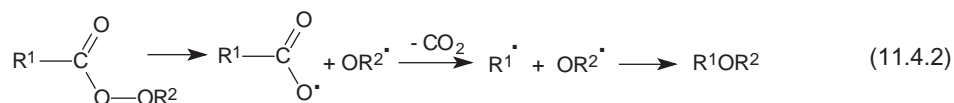
Thermal decomposition of acyl peroxides takes place at low temperatures and cannot be classified as pyrolysis. In many instances the thermal decomposition process takes place in a solvent. The decomposition of these compounds occurs with formation of free radicals. Free radical formation at a low temperature explains the utilization of these compounds (similar to that of other peroxides) as radical initiators in polymerization reactions. The activation energies in various reactions with the cleavage of the O–O bond are around 35 kcal/mol, depending on the attached acyl radicals [28,29]. For each peroxide, secondary reactions take place after the first step of O–O cleavage.

Peroxy acids generate, by thermal decomposition, chiefly  $\text{CO}_2$  and an alcohol, following the reaction indicated below:



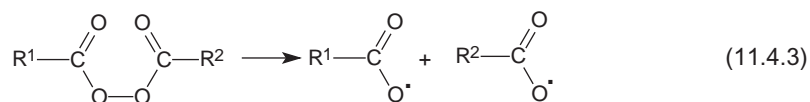


Peroxy esters are common polymerization initiators [30]. These compounds decompose with the formation of two free radicals, and the main reaction is the formation of an ether, as shown below:

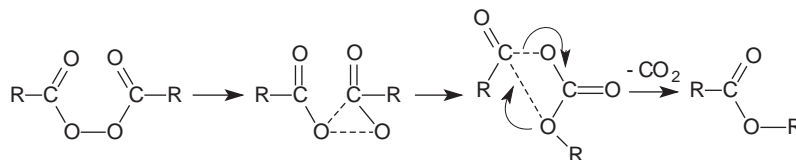


Various other reactions take place between the generated free radicals; the end result of the decomposition being a mixture of ethers, esters, and hydrocarbons.

Various studies were performed on thermal decomposition of diacyl peroxides, such as acetyl peroxide [31,32], acetyl propionyl peroxide [33], benzoyl peroxide [34–36], substituted benzoyl peroxides [37], lauroyl peroxide, decanoyl peroxide, octanoyl peroxide [29], and 1-apocamphoryl benzoyl peroxide [38]. For diacyl peroxides, the initial reaction is the cleavage of O–O bond similar to the other peroxides:



The elimination of  $\text{CO}_2$  from the radicals generated in reaction 11.4.3 also lead to the formation of free radicals  $\text{R}^1^\bullet$  and  $\text{R}^2^\bullet$ . Further interactions between all those free radicals lead to a mixture of reaction products. For example, acetyl peroxide generates  $\text{CO}_2$ , ethane, other alkanes, alkenes, methyl acetate, etc. Benzoyl peroxide generates benzoic acid, phenyl benzoate, biphenyl, benzene,  $\text{CO}_2$ , terphenyls, etc. When the reaction is performed in a solvent, reaction products involving the solvent molecules are also generated [39]. For some peroxides, such as  $\delta$ -phenylvaleryl peroxide, a carboxy inversion also seems to be involved, in part, in the decomposition process [32]. This reaction takes place as shown below:



Various other studies have been performed on diacyl peroxides thermal decomposition, typically related to their use as polymerization initiators [40]. Also, kinetic data for various decompositions are provided in the literature [29]. More complex acyl peroxides have been studied as well [41].

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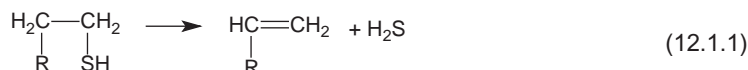
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## CHAPTER 12

*Pyrolysis of Thiols and Sulfides***12.1. THIOLS****General aspects**

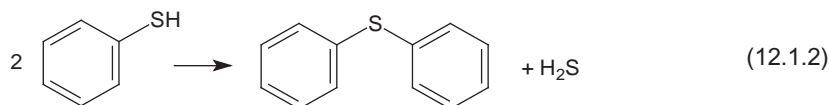
Thiols contain one or more SH groups in their molecule and can be considered analogs of alcohols, generated by replacing the OH group with SH. The IUPAC name of thiols is made by adding the suffix *thiol* to the name of the corresponding hydrocarbon (methanethiol for  $\text{CH}_3\text{-SH}$ , benzenethiol for  $\text{C}_6\text{H}_5\text{-SH}$ , etc.). Other names for thiols are also in use, such as mercaptans (methyl mercaptan for  $\text{CH}_3\text{-SH}$ ). Thiols are found in nature mainly in more complex combinations. Cysteine, for example, is a common amino acid having a SH group. Volatile thiols are known for their strong odor. As an example, 1-butanethiol has an odor threshold of 6 ppb in water and a flavor threshold of 0.004 ppb.

There is limited information available on thiols' pyrolysis. The stability to higher temperatures of thiols is similar to that of alcohols. Also, similar to some alcohols that eliminate water by pyrolysis, a number of thiols eliminate  $\text{H}_2\text{S}$  (see reaction 9.1.4). The elimination of  $\text{H}_2\text{S}$  is shown below for a thiol with hydrogen available to the carbons in  $\alpha$ - and  $\beta$ -position to the SH group:



The temperature of thiol decomposition depends on its structure. As an example, 3-methylbutan-1-thiol starts decomposing around  $500^\circ\text{C}$  [1]. For thiols, the equivalent of  $\text{H}_2$  elimination occurring for alcohols (see reaction 9.1.2) does not lead to the formation of thioaldehydes. Thioaldehydes are reactive compounds with a high tendency to form trimers and other condensation products, which decompose more easily than thiols. For this reason, some thiols, particularly those for which reaction 12.1.1 is not possible, generate by pyrolysis sulfur, larger-molecular-weight hydrocarbons, and other condensation products. At higher temperatures, formation of thiophene from thiols is also noticed [1].

Aromatic thiols are compounds stable to heating. For example, pyrolysis of benzenethiol does not start below  $500^\circ\text{C}$  and does not take place following reaction 12.1.1. The pyrolysis typically generates a mixture of compounds, and the formation of sulfides is one of the major decomposition paths. This reaction is shown below:



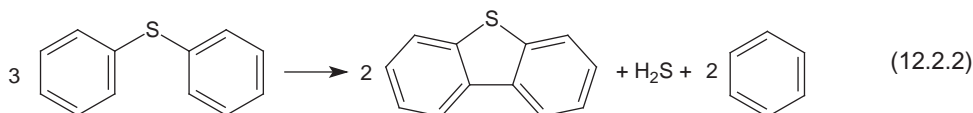
The variation in the remaining level of benzenethiol and the formation of phenylthiobenzene and benzene in the range  $600\text{--}700^\circ\text{C}$  in a flow experiment with 5.6 s contact time [2] are shown in Figure 12.1.1. The composition of the pyrolysate at  $700^\circ\text{C}$  was found to be 13% undecomposed benzenethiol, 16% benzene, 13% phenylthiobenzene, 2.3% diphenyl disulfide, 0.02% biphenyl, 0.5% diphenyl trisulfide, 0.3% dibenzo-thiophene, and less than 0.01% thianthrene. Similar results were obtained in a flash vacuum experiment. Other aromatic thiols behave similarly, as experimentally proven for 4-methyl-benzenethiol [2]. The reaction mechanism for the decomposition is very likely radicalic, with the cleavage of the C-S bond and termination reactions between the aryl free radicals.

The formation of sulfur bridges and  $\text{H}_2\text{S}$  elimination can be used for the synthesis of cyclic strained compounds [3]. One example is the synthesis of sulflower compound by flash vacuum pyrolysis



One explanation for this type of reaction is caused by the instability of thioaldehydes and thioketones, which cannot be isolated in pyrolysates. However, for some sulfides (e.g., diethylsulfide) thiols were found in the pyrolysate.

In the case of sulfides that cannot generate an alkene since no hydrogen is available on the  $\beta$ -carbon, pyrolysis typically leads to mixtures of compounds, the result depending on the molecular structure of the parent molecule. For example, pyrolysis of dibenzyl sulfide leads to the formation of toluene, stilbene, bibenzyl,  $\text{H}_2\text{S}$ , and other fragment molecules [1,4]. Diphenyl sulfide is very stable to pyrolysis, and at higher temperatures it generates as main reaction products  $\text{H}_2\text{S}$ , benzene, and diphenylene sulfide as shown below:



Some other sulfides deposit sulfur besides forming  $\text{H}_2\text{S}$  during pyrolysis.

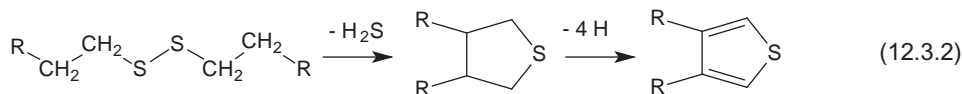
### 12.3. DISULFIDES

#### General aspects

Disulfides are compounds with the general formula  $\text{R-S-S-R'}$ . These compounds are more stable than the corresponding peroxides that contain the  $\text{O-O}$  group. When the R and R' are aliphatic radicals with two to five carbons, these compounds decompose in the range of temperatures  $300\text{--}500^\circ\text{C}$ . The reaction products include  $\text{H}_2\text{S}$ ,  $\text{R-SH}$  (and  $\text{R'-SH}$ ), sulfur ( $\text{S}_8$ ), sulfides, trisulfides, thiophane, thiophene, substituted thiophanes and thiophenes, alkanes, and alkenes [4]. The formation of sulfur can be explained by the reaction:



The formation of substituted thiophanes and thiophenes takes place by the following reaction:



The formation of  $\text{H}_2$  is not detected in the pyrolysate as a result of reaction 12.3.2, the dehydrogenation reaction of thiophane taking place simultaneously with reduction reactions that use the hydrogen to generate, for example, alkanes.

Some disulfides decompose at lower temperatures than those containing small hydrocarbon radicals. For example, dibenzyl disulfide decomposes at around  $200^\circ\text{C}$  to generate sulfur, stilbene, and a mixture of other compounds [1].

### 12.4. REFERENCES

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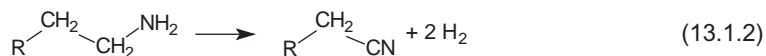
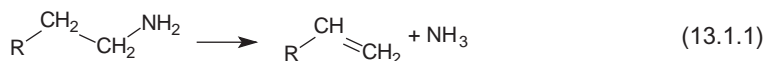
## CHAPTER 13

*Pyrolysis of Amines and Imines***13.1. PRIMARY AMINES****General aspects**

Primary amines can be considered as compounds derived from ammonia by the substitution of a hydrogen atom with an organic radical alkyl or aryl, or as compounds resulting from the substitution of a hydrogen atom from an organic molecule with the group  $\text{NH}_2$ . The general formula of primary amines is  $\text{R-NH}_2$  (for aromatic primary amines the formula  $\text{Ar-NH}_2$  is sometimes used). Continuing the substitution of hydrogens from ammonia with alkyl or aryl organic radicals, secondary amines ( $\text{R}_2\text{NH}$ ) and tertiary amines ( $\text{R}_3\text{N}$ ) are generated. The formation of quaternary ammonium cations ( $\text{NR}_4^+$ ) is also possible, these compounds being the equivalent of  $\text{NH}_4^+$  ion having the hydrogen substituted with organic radicals. The amines are named either using the name of the organic radical with the suffix *amine* (e.g., methylamine for  $\text{CH}_3\text{-NH}_2$ ) or using the prefix *amino* followed by the name of the hydrocarbon (e.g., aminomethane for  $\text{CH}_3\text{-NH}_2$ ). The substitution of a hydrogen from ammonia with an acyl radical ( $\text{R-C(O)-}$ ) leads to the formation of amides. Amides can be considered derivatives of acids, and their pyrolysis is discussed in Chapter 20. Amine oxides can also be considered compounds different from amines and are discussed in Section 14.4.

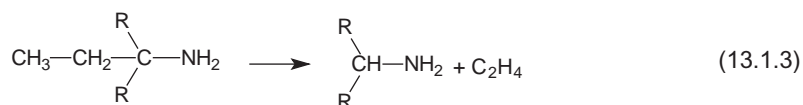
**Aliphatic primary amines**

Aliphatic primary amines have a carbon with  $\text{sp}^3$  hybridization and two hydrogen atoms connected to the nitrogen atom. Pyrolysis of these compounds can take place with the involvement of the  $\text{NH}_2$  group. In this case, there are two common paths, one with ammonia elimination and formation of an unsaturated hydrocarbon (similar to water elimination in alcohols) and the other with hydrogen elimination and formation of a nitrile. These two types of reactions are shown below:



Other reactions involving the amino group were also noticed during pyrolysis of some amines, such as generation of  $\text{HCN}$ ,  $\text{N}_2$ , etc. As temperatures of the pyrolysis increase, the formation of small molecules such as  $\text{HCN}$  is favored.

Pyrolysis of amines can also occur with the cleavage of a  $\text{C-C}$  bond and not involving the  $\text{NH}_2$  group. This happens more frequently when a  $\text{C-C}$  bond has a dissociation energy close to that of the  $\text{C-N}$  bond, such as when the amine molecule contains a tertiary carbon atom. This type of reaction is shown as follows:



From Table 3.1.2 it can be seen that dissociation energy for the bond  $\text{NH}_2\text{-CR}_3$  is about 77.2 kcal/mol, and for the bond  $\text{C}_2\text{H}_5\text{-CR}_3$  is about 76.9 kcal/mol. Because the two dissociation energies are so

close, reaction 13.1.3 is a likely process. The C–C bonds involving only primary or secondary carbons have slightly higher dissociation energies, and their cleavage compared to C–N bond cleavage is less favored.

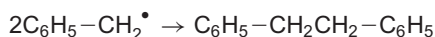
Pyrolysis of ethylamine generates in the temperature range 500–1000 °C mainly CH<sub>3</sub>CN, H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and NH<sub>3</sub>, following the main reactions 13.1.1 and 13.1.2. The ratio of different components varies as a function of temperature, the level of ethylene decreasing as the temperature increases. Besides these four main reaction products, traces of HCN and some N<sub>2</sub> were also detected in ethylamine pyrolysate.

Pyrolysis of propylamine follows a path very similar to that of ethylamine. The formation of propylene, however, is associated with the formation of some ethylene, showing that the C–C bond can also break during pyrolysis of propylamine. In addition to the presence of smaller hydrocarbons, pyrolysis of short-chain amines shows the possible formation of higher molecular weight hydrocarbons. These heavier hydrocarbons are the result of termination reactions between the radicals formed during pyrolysis.

A detailed study regarding short-chain primary amine pyrolysis has been done on 2-methylbut-2-ylamine (*tert*-amylamine) [1]. The study was done using single-pulse shock-tube pyrolysis on *tert*-amylamine in concentrations between 0.1% and 0.4%, in the presence of toluene (1%) or cyclohexene (0.01%) diluted with argon. The study determined the rate constants and Arrhenius equations for the formation of NH<sub>2</sub><sup>•</sup> free radicals and C<sub>2</sub>H<sub>5</sub><sup>•</sup> free radicals from *tert*-amylamine. The results regarding the formation of NH<sub>3</sub> and C<sub>5</sub>H<sub>10</sub> from *tert*-amylamine suggest that the maximum values for *k* can be expressed in the form  $k \text{ (s}^{-1}\text{)} \leq 10^{14.5} \exp(-37,200/T)$ . Kinetic information is also available in the literature for the pyrolysis of other amines such as benzylamine [2,3] and *tert*-butylamine [4]. The decomposition of benzylamine studied in a flow through reactor with toluene as a carrier gas generates NH<sub>3</sub> and (2-phenylethyl)-benzene (dibenzyl). The first step in this reaction is the formation of free radicals as shown below:



The toluene present as a carrier is involved in the chemical reaction as shown below:

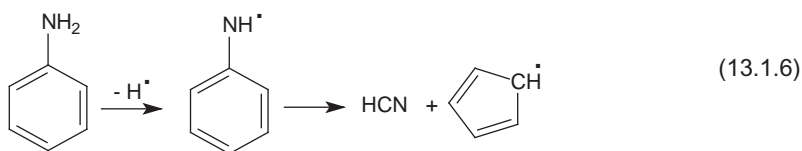


The kinetics of the decomposition reaction in the temperature range 650–800 °C was determined to follow Arrhenius equation:

$$k \text{ (s}^{-1}\text{)} = 6 \times 10^{12} \exp\left[\frac{-59000 \text{ (cal)}}{RT}\right] \quad (13.1.5)$$

### Aromatic primary amines

Aromatic primary amines, such as aniline, are thermally stable compounds. At temperatures above 700 °C, aniline starts decomposing with the formation of benzene, N<sub>2</sub>, HCN, and other molecules including low levels of carbazole. Several reaction mechanisms were proposed for the formation of different pyrolysis products. The cleavage of C<sub>6</sub>H<sub>5</sub>NH–H bond with the formation of C<sub>6</sub>H<sub>5</sub>NH<sup>•</sup> (anilino radical) and a hydrogen atom was estimated to be about 86.4 ± 2 kcal/mol [5]. The formation of C<sub>6</sub>H<sub>5</sub>NH<sup>•</sup> is followed by other reactions, such as generation of HCN and cyclopentadienyl radical as shown below:



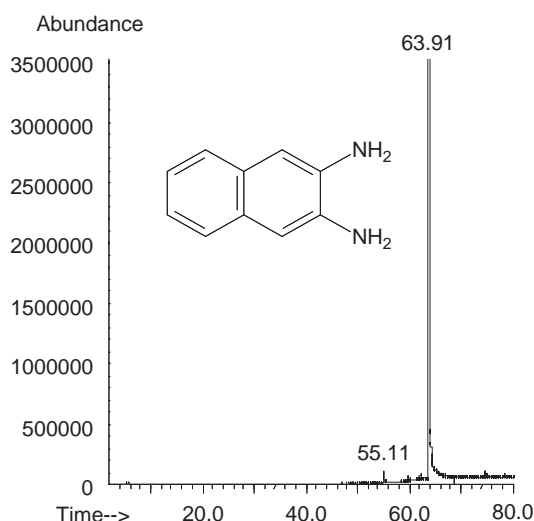
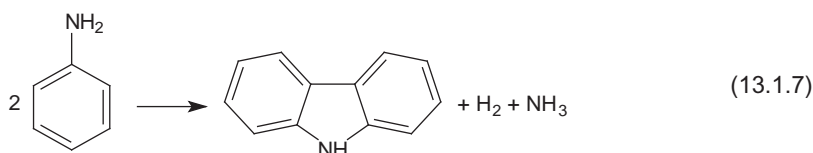


FIGURE 13.1.1. Pyrogram of 2,4-diaminonaphthalene at 900 °C.

Cyclopentadienyl radical can be an intermediary species for the formation of various aromatic hydrocarbons, as shown in Section 7.5. The reaction of carbazole formation, also involving the anilino radical, can be written as follows:



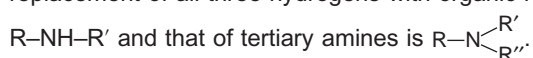
Other aromatic primary amines are also stable compounds at temperatures up to 700–800 °C. 2,2'-Diaminobiphenyl by pyrolysis above 800 °C generates a complex mixture of compounds that contains aromatic hydrocarbons including anthracene. Pyrolysis of 2,3-diaminonaphthalene performed on 1.0 mg compound using Type 3 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900$  °C,  $\beta = 10$  °C/ms, THT = 10 s, and housing temperature  $T_{\text{hou}} = 280$  °C, showed practically no decomposition. The pyrogram is shown in Figure 13.1.1.

The peak from the pyrogram eluting at 63.91 min is generated by the parent compound. The peak at 55.11 min belongs to 1-aminonaphthalene, which was present as an impurity in the initial sample. The high thermal stability of aromatic amines also explains the formation of compounds from this group, such as 4-aminobiphenyl, and of 1- and 2-aminonaphthalene, in different burning processes where nitrogenous compounds are present [6–8].

## 13.2. SECONDARY AND TERTIARY AMINES

### General aspects

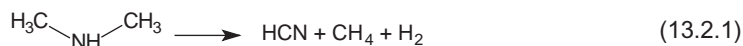
Secondary amines can be considered as compounds derived from ammonia by the replacement of two hydrogens with organic radicals, and tertiary amines can be considered as derived from ammonia by the replacement of all three hydrogens with organic radicals. The general formula of secondary amines is



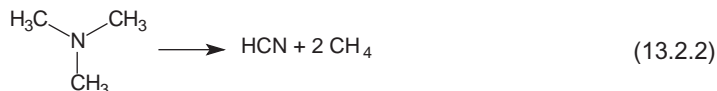


**Aliphatic amines**

Secondary and tertiary aliphatic amines are, in general, compounds stable to heating. For example, dimethylamine ( $\text{CH}_3)_2\text{NH}$  decomposes at temperatures above  $800^\circ\text{C}$  to generate HCN,  $\text{CH}_4$ , and  $\text{H}_2$  by the following reaction:



Similarly, trimethylamine decomposes at high temperatures into  $\text{CH}_4$  and HCN.



Diethylamine and triethylamine decompose similarly at temperatures around  $1200^\circ\text{C}$  to generate HCN,  $\text{CH}_4$ , low levels of other hydrocarbons, and also char. Due to the high stability of N–C bond, the amines with substituents to the nitrogen atom, which are less stable to heating, will undergo decompositions of the substituent moiety, sometimes before the cleavage of the N–C bond.

**Cyclic saturated amines**

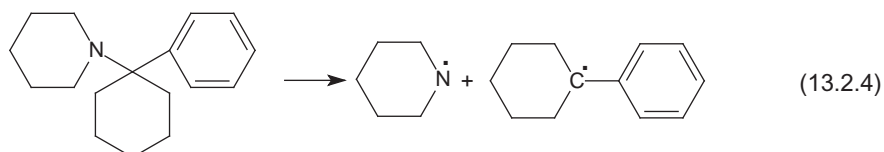
Cyclic saturated amines are secondary or tertiary amines. These compounds can be considered saturated (nonaromatic) heterocycles. Among the most common cyclic saturated amines are pyrrolidine (tetrahydropyrrole), which contains a five-member ring, and piperidine (hexahydropyridine) with a six-member ring. Thermal decomposition of pyrrolidine has been studied in the temperature range  $900\text{--}1400\text{ K}$  using single-pulse shock waves [9]. The experiment was performed on a diluted compound 1% in argon and had an overall density of  $3 \times 10^{-5} \text{ mol/cm}^3$ . Under these conditions, the pyrolysis products detected post shock included:  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$ ,  $\text{CH}_2=\text{C}=\text{CH}_2$ ,  $\text{CH}_3\text{C}\equiv\text{CH}$ ,  $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ , HCN,  $\text{CH}_3\text{CN}$ ,  $\text{CH}_2=\text{CHCN}$ ,  $\text{C}_2\text{H}_5\text{CN}$ , and small quantities of pyrrole and butadiene. It was demonstrated that  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  were produced directly by the ring cleavage as shown below for the formation of  $\text{C}_2\text{H}_4$ :



Several Arrhenius parameters were established for individual concurrent reactions that occur during pyrolysis. These include the reaction  $\text{pyrrolidine} \rightarrow \text{C}_2\text{H}_4 + \text{aziridine}$  with  $A = 3.42 \times 10^{16}$  and  $E^\ddagger = 75.2 \times 10^3 \text{ cal}$ , and the reaction  $\text{pyrrolidine} \rightarrow \text{C}_3\text{H}_6 + \text{CH}_2=\text{NH}$  with  $A = 1.35 \times 10^{16}$  and  $E^\ddagger = 80.4 \times 10^3 \text{ cal}$ . The compound at the highest concentration in the pyrolysate among the nitrogenous compounds was HCN followed by  $\text{CH}_3\text{CN}$ . During pyrolysis, no isomerization reaction of pyrrolidine was noticed.

Piperidine decomposes by similar reactions as pyrrolidine. A compound that contains a piperidine ring substituted at the nitrogen atom is 1-(1-phenylcyclohexyl)piperidine or phenylcyclohexyl (PCP). PCP is a Schedule II drug with a high potential for drug abuse. Pyrolysis of this compound performed in a Vycor tube at  $400$ ,  $600$ , and  $800^\circ\text{C}$  is reported in the literature [10]. Around  $400^\circ\text{C}$  only 30–40% of PCP is decomposed, generating phenylcyclohexane, phenylcyclohexene, piperidine, and 2,3,4,5-tetrahydropyridine. Most of the compound is decomposed at  $600^\circ\text{C}$ . As the temperature increases from  $400^\circ\text{C}$  toward  $800^\circ\text{C}$ , the level of HCN increases from 0% to 2.3% at  $600^\circ\text{C}$  and to 5.1% at  $800^\circ\text{C}$ . The pyrolysis products include aromatic hydrocarbons with three or fewer rings (95–97%) such as styrene, methylstyrene, methylindenes, naphthalene, biphenyl, and phenanthrene. Also, the pyrolysate contains PAHs (1–2%), aza-arenes, and bases. The aza-arenes and bases include methylpyridines, methylquinolines, isoquinolines, benzo[*h*]quinoline, 2-phenylquinoline, a methylphenylquinoline, etc.

The composition of pyrolysate can be explained by the initial formation of free radicals in a reaction as shown below:

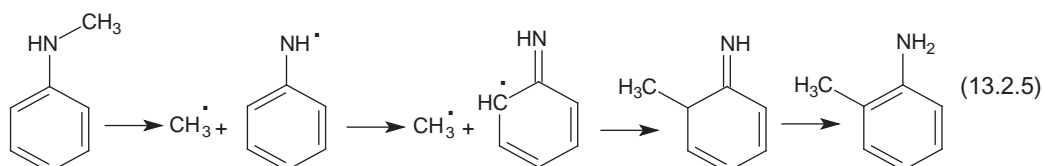


Further reactions of the phenylcyclohexyl free radical explain the formation of aromatic hydrocarbons (including PAHs). Piperidinyl *N*-radical can decompose further to form HCN and small hydrocarbons or can undergo condensation reactions to form aza-arenes.

Pyrolysis of other compounds containing a piperidine ring has been reported in connection with amine light stabilizers used in polymers [11]. Piperidine rings connected to other molecule moieties were shown to generate, above 700 °C, pyridine rings by dehydrogenation.

### Aromatic secondary and tertiary amines

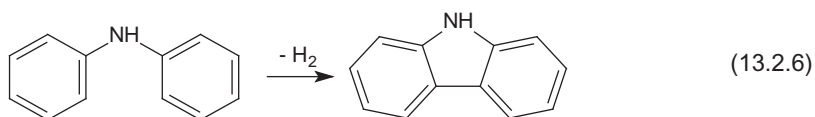
Aromatic secondary and tertiary amines are also stable upon heating [12–14]. The decomposition of *N*-methylaniline takes place with the formation of HCN, benzene, aniline, and also *o*- and *p*-toluidine and other fragment molecules [15]. The dissociation for the  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)-\text{H}$  bond with the formation of  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)^\bullet$  (*N*-methylanilino radical) and a hydrogen atom was estimated to be about  $84.9 \pm 2$  kcal/mol [5]. The dissociation of  $\text{C}_6\text{H}_5\text{NH}-\text{CH}_3$  bond with the formation of  $\text{C}_6\text{H}_5\text{NH}^\bullet$  and  $\text{CH}_3^\bullet$  radicals was estimated to be about  $75 \pm 4$  kcal/mol and therefore favored compared to the formation of hydrogen atoms. This reaction is probably responsible for the migration of the alkyl group from the nitrogen atom to the benzene ring during pyrolysis to generate the toluidines. The formation of *o*-toluidine is shown below:



The possibility of the cleavage during pyrolysis of  $\text{C}_6\text{H}_5-\text{NHCH}_3$  bond should not be eliminated, the presence of the unstable  $\text{CH}_2=\text{NH}$  species during pyrolysis being demonstrated by infrared spectroscopic measurements [16].

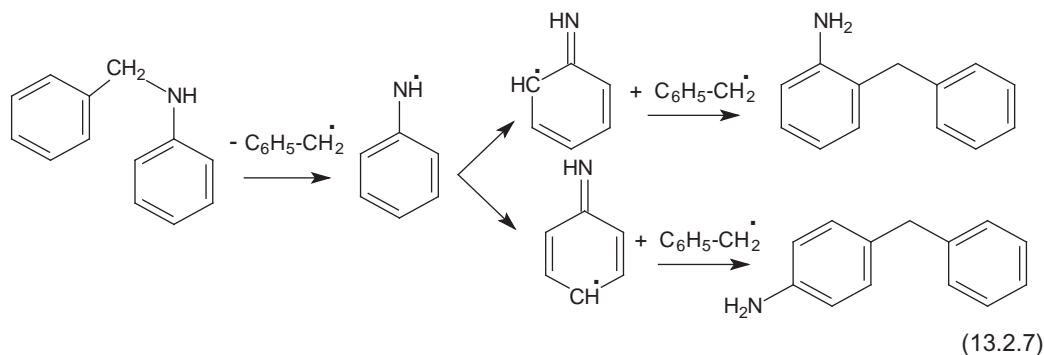
*N*-Ethylaniline (ethylphenylamine) pyrolysis also takes place at temperatures above 800 °C with the formation of a complex mixture containing HCN, benzene,  $\text{NH}_3$ , aniline substituted at the aromatic ring, low levels of indole, and char. Dimethylaniline at temperatures above 1000 °C generates benzonitrile,  $\text{NH}_3$ , benzene, HCN, and char.

Diphenylamine by pyrolysis at temperatures above 800 °C generates a mixture of compounds, including carbazole, in a reaction as shown below:

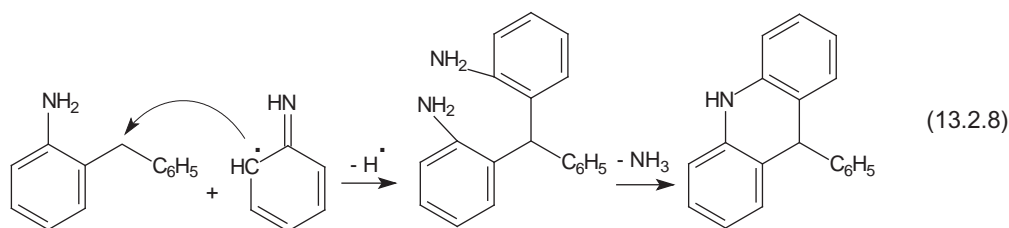


*N*-Benzylaniline (phenylbenzylamine), on the other hand, decomposes at lower temperatures. When heated at 315 °C for an extended period of time (100 h) in a sealed tube in a nitrogen atmosphere, *N*-benzylaniline generates a mixture of  $\text{NH}_3$ , aniline, toluene, biphenyl, diphenylmethane, dibenzyl, *trans*-stilbene, *o*- and *p*-amino-diphenylmethane, 9-phenylacridine, 2,3-diphenylindole, and char. A first step in the pyrolysis is very likely the cleavage of the bond  $\text{C}_6\text{H}_5\text{NH}-\text{CH}_2\text{C}_6\text{H}_5$  with the formation of two

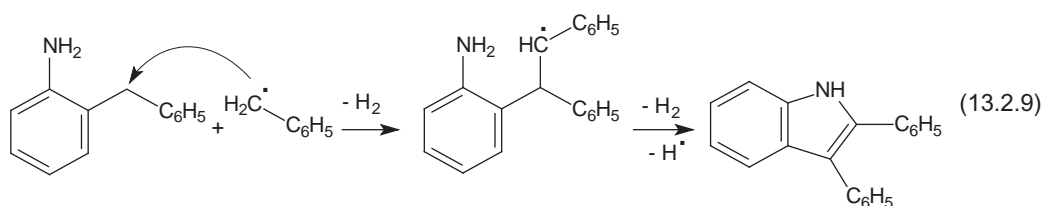
free radicals  $\text{C}_6\text{H}_5\text{NH}^\bullet$  and  $\text{C}_6\text{H}_5\text{CH}_2^\bullet$ . These radicals by different subsequent reactions generate the pyrolysate components. As an example, the reactions for the formation of *o*- and *p*-aminodiphenylmethane can be written as follows:



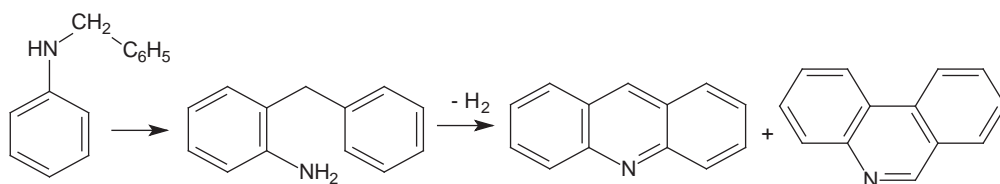
The formation of 9-phenylacridine can be explained starting with a molecule of *o*-aminodiphenylmethane and  $\text{C}_6\text{H}_5\text{-NH}^\bullet$  free radical, shown to be generated in the following reaction:



The formation of 2,3-diphenylindole can be explained by different reactions, either starting with stilbene and  $\text{C}_6\text{H}_5\text{-NH}^\bullet$  free radical [13], or starting with *o*-aminodiphenylmethane and  $\text{C}_6\text{H}_5\text{-CH}_2^\bullet$  free radical. This second possible reaction is shown below:

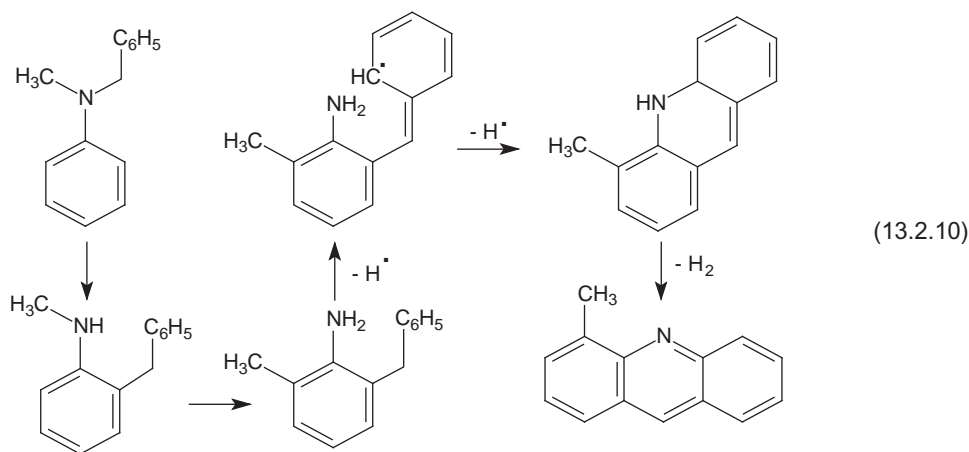


At higher temperatures, *N*-benzylaniline generates among other compounds acridine and lower levels of phenanthrydine in a reaction as shown below:



The stability of the heterocyclic aromatic compounds at higher temperatures favors the formation of these compounds.

*N*-Benzyl-*N*-methylaniline decomposes at lower temperatures around 315 °C and extended heating time (100 h) similar to *N*-benzylaniline [12]. The reaction products in this case consist of a mixture of compounds including diphenylmethane, dibenzyl, *o*-toluidine, methylamine, 4-methylacridine, and benzylquinolone. The formation of benzyl and *N*-methylanilino free radicals is probably the first step during pyrolysis. The migration of the benzyl group from the nitrogen atom to the benzene ring is part of the reaction generating the pyrolysis products, in a similar manner as for benzylaniline. The methyl radical can also migrate to the benzene ring. Potential reactions leading to the formation of 4-methylacridine are shown below:

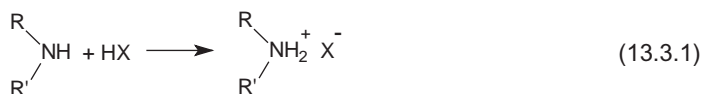


The formation of the other pyrolysate constituents can be explained easily by the combination of various radicals generated from the parent molecule [17].

### 13.3. SALTS OF AMINES

#### General aspects

Amines are compounds with a basic character similar to ammonia. Under the influence of an acid, they can form salts in a reaction shown below for a secondary amine:

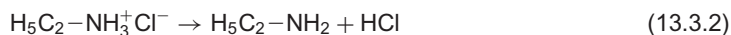


Pyrolysis of amine salts can lead to different results than those of their free amine base when certain pyrolysis procedures are used. In flash pyrolysis, for example, as the temperature increases, the volatile compounds can be swept rather quickly outside the heating zone by a carrier gas. This process may take place even for the parent compound. For volatile compounds pyrolyzed in instruments dedicated for solid samples, either being parent compound or pyrolysate constituent, the true exposure time to the elevated temperature can be much shorter than the heating time set for the pyrolysis instrument. Since the amine salts are not volatile while the corresponding free bases may be volatile, the two types of compounds can be heated differently, even when the instrument settings are the same. Different heating may lead to a different composition of the pyrolysates of the two compounds. However, this is not the typical case, for example, for the case of pyrolysis in a sealed tube.

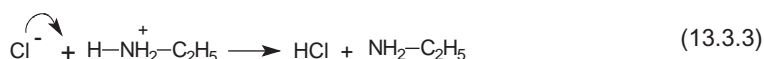
Besides the differences caused by the potential heating time experienced by the sample during pyrolysis, for some amines there are differences between the free amine pyrolysate and its salt pyrolysate. One such difference consists of lower temperatures necessary to achieve the same decomposition rate of the parent molecule. However, for some other amines, when pyrolysis is truly

performed in similar conditions, the pyrolysate composition for amine salts can be similar to that for the free amine.

For the salts of inorganic acids, a common reaction during pyrolysis is the elimination of HX from the salt. This reaction is shown below for ethyl ammonium chloride:



The mechanism of this reaction can be considered to be that of a typical nucleophilic substitution:

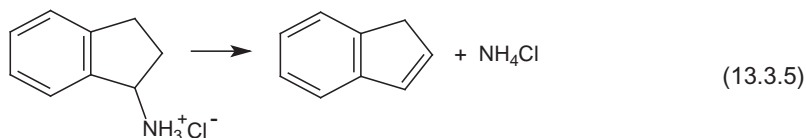


In the case of further decomposition of the free amine generated in reaction 13.3.2, the result of pyrolysis for the salt can be similar to that of the free amine (see reactions 13.1.1 and 13.1.2). The reaction with the formation of an alkene is shown below for the case of ethyl ammonium chloride:



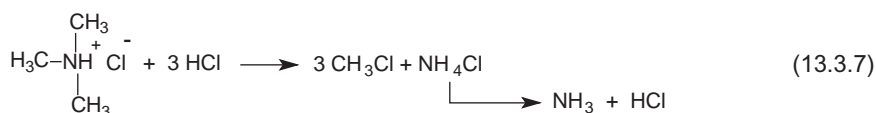
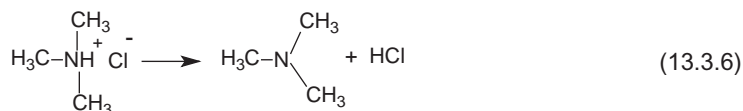
In fact, ethyl ammonium chloride forms by pyrolysis in part ethylamine and HCl, and in part ethylene and  $\text{NH}_4\text{Cl}$ .

The formation of a free amine as an intermediate step during pyrolysis is not necessary for the production of similar compounds from the salt and the free amine. The formation of compounds with double bonds by  $\text{NH}_4\text{Cl}$  elimination typically takes place at lower temperatures compared to the elimination of  $\text{NH}_3$ . Also, the chances for side reactions besides the alkene formation are reduced compared to the case of the pyrolysis of free amines. As an example, when 1-aminohydrindene hydrochloride is heated at  $250^\circ\text{C}$ , it generates indene and  $\text{NH}_4\text{Cl}$ , as shown in the reaction below:



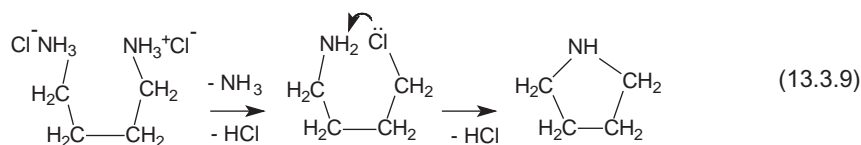
1-Aminohydrindene pyrolysis takes place at higher temperatures and with lower yield of indene. Other salts that behave similar to the free amine include, for example, *N*-methylaniline hydrochloride. This substance decomposes similarly with the free base with the formation of HCN, benzene, aniline, and also of *o*- and *p*-toluidine and other fragment molecules [15]. Hydrochloric acid is also formed during pyrolysis of the salt.

On the other hand, trimethylammonium chloride by pyrolysis generates a more complex mixture of compounds compared to those formed in reaction 3.2.2 from the free base. At temperatures around  $350^\circ\text{C}$ , trimethylammonium chloride forms trimethylamine and HCl, and also methylamine, methyl chloride, etc. Some reactions taking place during the decomposition of trimethylammonium chloride are shown below:

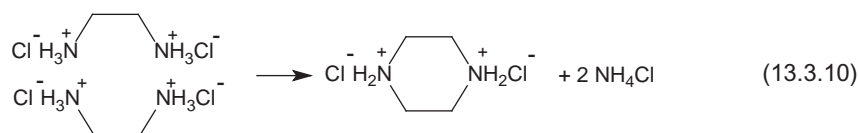


The nature of the inorganic ion that forms the salt may influence the pyrolysis result (see, e.g., [12]).

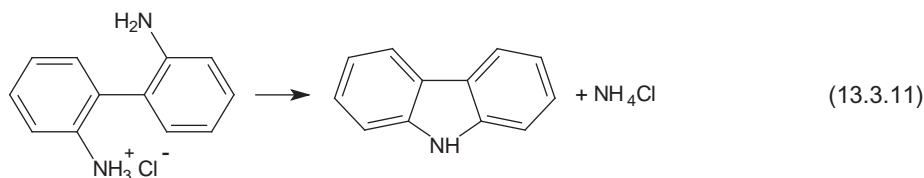
The formation of  $\text{NH}_4\text{Cl}$  in the pyrolysis of salts of various amines has been applied successfully for the preparation of some heterocycles. Pyrolysis of diamine hydrochlorides with the amino groups separated by four or more atoms leads to the formation of cyclic amines. For example, 1,4-butanedi-amine (putrescine) dihydrochloride generates by pyrolysis pyrrolidine. Similarly, 1,5-pentandiamine (cadaverine) dihydrochloride forms piperidine. The reaction is shown below for putrescine:



The mechanism of these reactions is that of nucleophilic substitutions. For ethylenediamine hydrochloride the elimination is intermolecular and leads to piperazine, as shown in the following reaction:



The elimination of  $\text{NH}_4\text{Cl}$  from diamine salts can also be applied for the synthesis of other cycles containing nitrogen, such as tetrahydroisoquinoline starting with [2-(amino-methyl)phenyl]methanamine hydrochloride (*o*-xylylenediamine hydrochloride). The elimination of  $\text{NH}_4\text{Cl}$  may be achieved even from salts of diamines with only one amine group in salt form. This is shown below for the pyrolysis of 2,2'-diaminobiphenyl mono hydrochloride, which generates carbazole by pyrolysis:



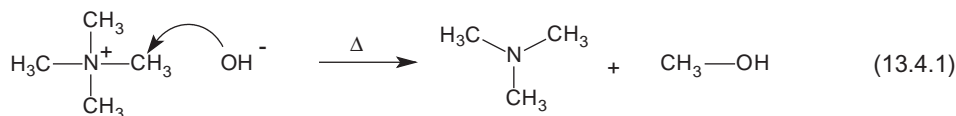
### 13.4. QUATERNARY AMMONIUM HYDROXIDES AND SALTS

#### General aspects

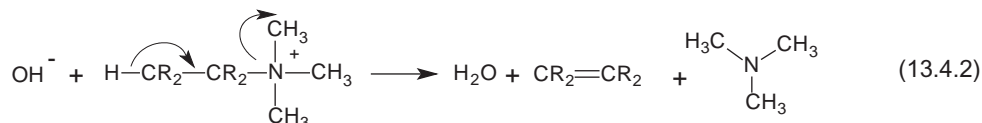
Quaternary ammonium hydroxides have the general formula  $\text{NR}_4^+\text{OH}^-$ , and quaternary ammonium salts have the general formula  $\text{NR}_4^+\text{X}^-$  (where  $\text{X}^-$  is an inorganic or organic anion and R is an organic radical). These compounds can be considered as generated by the replacement of the hydrogens in the ammonium ion  $\text{NH}_4^+$  with organic radicals. Similar to the other amines, different R substituents to the same nitrogen atom are possible.

#### Quaternary ammonium hydroxides

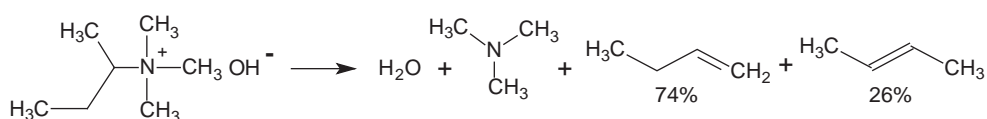
Thermal decomposition of quaternary ammonium hydroxides was discussed previously in Section 2.6 since these compounds are used as reagents in pyrolysis/alkylation techniques [18,19]. Pyrolysis of pure tetramethylammonium hydroxide (TMAH) generates mainly methanol and trimethylamine, as shown in the following reaction:



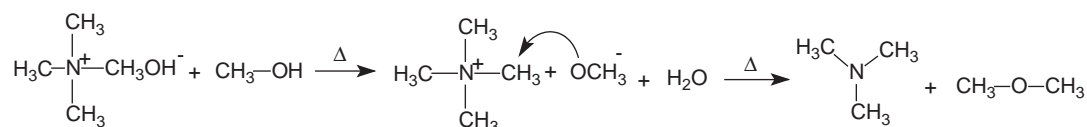
In some pyrolysis reactions instead of the formation of an alcohol, the result is the formation of water and an alkene. One example of this reaction is that of tetraethyl ammonium hydroxide, which generates by pyrolysis triethylamine,  $C_2H_4$ , and  $H_2O$ . The general reaction taking place with a bimolecular elimination mechanism can be written as follows:



In cases where different alkenes can result from the quaternary salt, the alkene with the smallest number of substituents at the double bond is typically preferred (Hofmann rule), as shown below for trimethyl(methylpropyl) ammonium hydroxide:



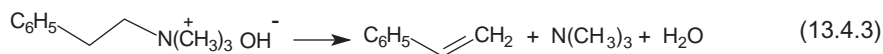
Other small molecules can be generated by the pyrolysis of tetramethylammonium hydroxide. For example, dimethyl ether can be formed by the following nucleophilic substitution (with  $S_N2$  mechanism) in a reaction between the quaternary salt and the methanol generated in the main reaction 13.4.1:



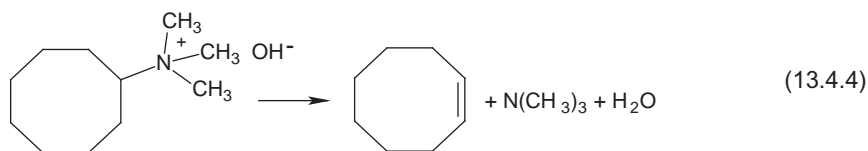
The ether is present at lower levels in the pyrolysates as compared to the alcohol.

Pyrolysis of quaternary ammonium hydroxides with different substituents shows the tendency to eliminate as an alcohol mainly the smallest radical. In the case of phenyl trimethyl ammonium hydroxide, for example, methanol is formed as a major reaction product. However, for a number of quaternary ammonium hydroxides with the general formula  $R(CH_3)_3N^+OH^-$ , the yield of methanol was found to vary considerably depending of the nature of the radical R [12].

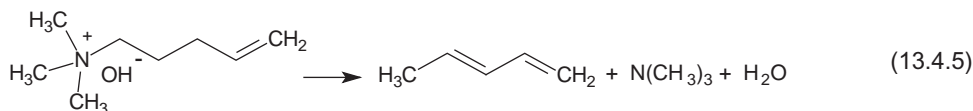
For quaternary ammonium hydroxides with different substituents at the nitrogen atom, the reaction leading to an alkene is also common. This reaction is shown below for phenylethyl trimethyl ammonium hydroxide, which by thermal decomposition forms styrene, trimethylamine, and water:



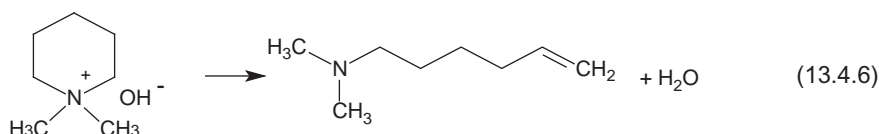
With unsymmetrical amines the major alkene product is the least substituted and generally the least stable one, an observation known as the Hofmann rule. This is in direct contrast to normal elimination reactions where the more substituted, stable product is dominant (Zaitsev's rule). Reaction 13.4.3 can be used to synthesize unsaturated cyclic compounds as shown below for the decomposition of cyclooctyltrimethylammonium hydroxide, which forms cyclooctene with good yields (60% *trans* and 40% *cis* form) in a reaction as shown below:



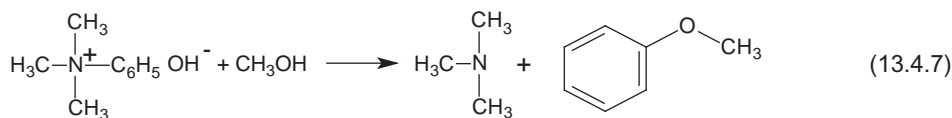
Reaction 13.4.3 applied to trimethyl pent-4-enylammonium hydroxide leads to the formation of a compound with a new double bond as expected, but the double bond migrates to form a conjugated system (penta-1,3-diene and not penta-1,4-diene is formed):



An interesting reaction takes place for the compounds where the nitrogen atom is part of a cycle, such as in the case of dimethyl piperidinium hydroxide, which reacts with the opening of the cycle as shown below:

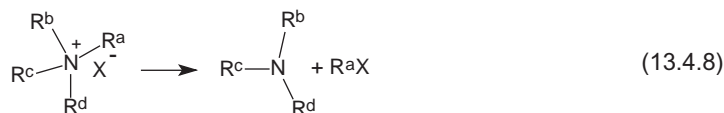


The ether formation (as in the case of TMAH) is also noticed for hydroxides with different substituents. For example, in the pyrolysis of phenyl trimethyl ammonium hydroxide, some anisole is formed. The initial decomposition of the compound generates *N,N*-dimethylaniline and methanol, followed by the reaction of methanol with the quaternary base as shown below:

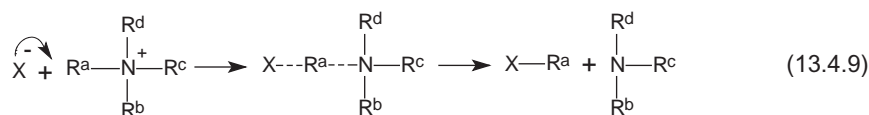


### Quaternary ammonium salts

Thermal decomposition of quaternary ammonium salts is in many respects similar to the decomposition of quaternary ammonium hydroxides. A typical decomposition for a salt with an inorganic anion takes place as shown below:



The formation of  $\text{R}^a\text{X}$  in reaction 13.4.8 is similar to reaction 13.4.1 (replacing OH with X). In the case of quaternary ammonium chloride, for example, the result of pyrolysis is a tertiary amine and a chlorinated hydrocarbon. Reaction 13.4.8 takes place as a nucleophilic substitution (see Section 2.5), as shown below:



In cases where the substituents to the nitrogen atom are not the same, there is the question of which radical will form the halide and which one will remain attached to the nitrogen. Typical for a nucleophilic substitution, the leaving group is eliminated from the quaternary ammonium salt more easily when the group is more stable, this stability being usually inverse to the group basicity. For this reason,



substituents like phenyl have the tendency to remain attached to the nitrogen, while groups like methyl have the tendency to form the RX molecule. Since  $R_3N$  is in general a very good leaving group regardless of the nature of R, the strength of the bond N–R also plays a role regarding which group remains attached to the nitrogen and which one becomes a leaving group. The typical order of tendency to remain attached to the nitrogen atom for the radicals R is the following: phenyl > vinyl > pentyl > butyl > propyl > ethyl > methyl > benzyl > allyl. For example, methyltriethyl-ammonium chloride generates mainly triethylamine and methyl chloride, and phenyl trimethyl ammonium chloride generates mainly dimethylphenylamine and methyl chloride.

Thermal decomposition of quaternary ammonium hydroxides and salts takes place more easily as the nucleophilicity of the anion is higher. For this reason, the decomposition temperature of quaternary ammonium compounds tends to be in the same order as nucleophilicity in gas phase of the anion, which is in the following order:  $OH^- > F^- > CH_3O^- > CH_3COO^- > Cl^- > CN^- > Br^-$  [20]. For example, tetramethylammonium fluoride decomposes around 180 °C, while tetramethylammonium chloride decomposes at 360 °C. The hydroxides decompose in general at lower temperatures than the salts, and the reaction is very rapid, which explains the success of using TMAH and other similar compounds in pyrolytic methylation (alkylation) reactions (see Section 2.6).

### 13.5. AMINES CONTAINING OTHER FUNCTIONAL GROUPS

#### *General aspects*

Besides the amino groups (primary, secondary, tertiary, or quaternary), other functional groups can be present in organic molecules. The subject of this section is the pyrolysis of organic compounds with amino and halogen groups, and with amino and OH groups. Other multifunctional organic compounds also containing amino groups are discussed further in this book (see, e.g., Section 16.3 for amino sugars, Chapter 19 for amino acids).

#### *Compounds with amino and halogen groups*

The reaction between amines and halogenated compounds is a well-known procedure for the addition of new substituents to the nitrogen atom, as shown below for the reaction of a primary amine:

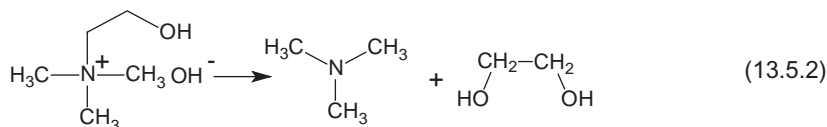


This reaction would be expected to take place even when the two groups  $NH_2$  and X are attached to the same molecule, unless the process is not possible for steric reasons. However, the formation of cyclic compounds using reaction 13.5.1, for example, to synthesize azacycloalkanes, is not the recommended path for the synthesis of these compounds. Although the reaction of a  $\alpha,\omega$ -dihalide with an amine has been used to obtain cyclic amines [21], the process does not involve pyrolytic conditions. Pyrolysis of 4-(2-chloroethyl)-phenylamine was reported initially to generate dihydro-*p*-indole [22], but the pyrolysis of 4-(3-chloropropyl)phenylamine did not generate the expected *p*-tetrahydroquinoline, and the formation of a *p*-indole by this pyrolysis reaction is questionable. 4-Chloropyridine (a heterocycle derivative) generates by heating 4-chloro-1-(4-pyridyl)-pyridinium chloride due to the high reactivity of chlorine in 4-chloropyridine.

#### *Compounds with amino and OH groups*

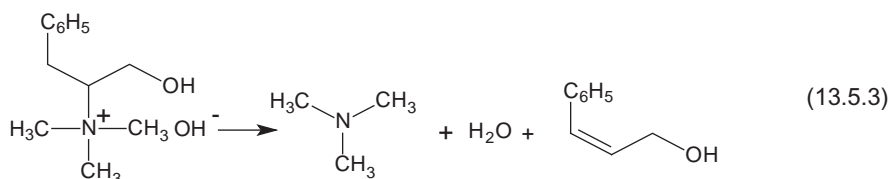
Among the molecules containing amino and OH groups, a well-known compound is choline, which is the cation (2-hydroxyethyl)trimethylammonium with different counterions ( $OH^-$ ,  $Cl^-$ , etc.). This compound plays an important physiological role in animals. Pyrolysis of choline hydroxide takes place mainly with

the formation of trimethylamine and ethylenediol as shown below:



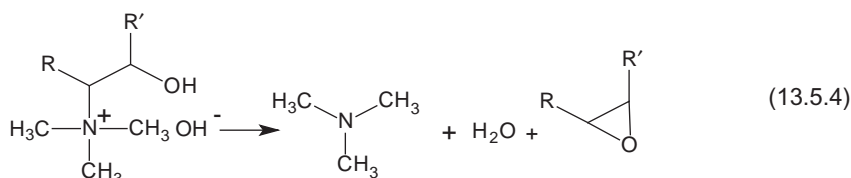
The formation of 2-(dimethylamino)ethan-1-ol and methanol also takes place, but to a lesser extent. Some of the 2-(dimethylamino)ethan-1-ol further eliminates water to form dimethylvinylamine.

Choline is the first member of a whole group of similar compounds with various substitutions at the ethyl moiety, the resulting compounds being known as cholines. Pyrolysis of these compounds typically generates water, trimethylamine, and the unsaturated alcohol. For example, [2-hydroxy-1-(benzyl)ethyl]trimethylammonium hydroxide decomposes as shown in the following reaction:



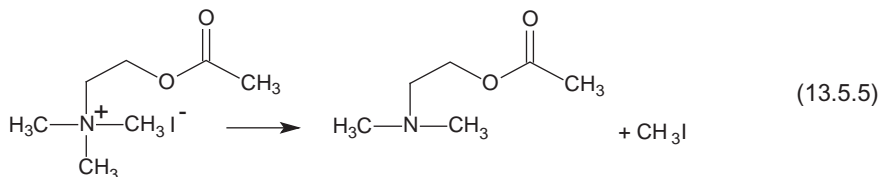
Reaction 13.5.3 is similar to the formation of water and an alkene as shown in reaction 13.4.2.

For some choline type compounds, instead of the formation of an alcohol with a double bond between  $\beta$  and  $\gamma$  carbons to the OH group, the result of pyrolysis is the formation of an epoxide, as shown in the following reaction:



In reaction 13.5.4, R and R' can consist of various combinations of H, alkyl, or aryl radicals such as (CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>), (n-C<sub>5</sub>H<sub>11</sub>, H), (CH<sub>2</sub>-CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, H), (cyc-C<sub>6</sub>H<sub>11</sub>, H), etc., for (R, R'), respectively [12].

A compound related to choline is acetylcholine, an important neurotransmitter in many organisms including humans. Thermal decomposition of acetylcholine iodide has been used for analytical purposes [23] in the determination of acetylcholine and takes place by the following reaction:

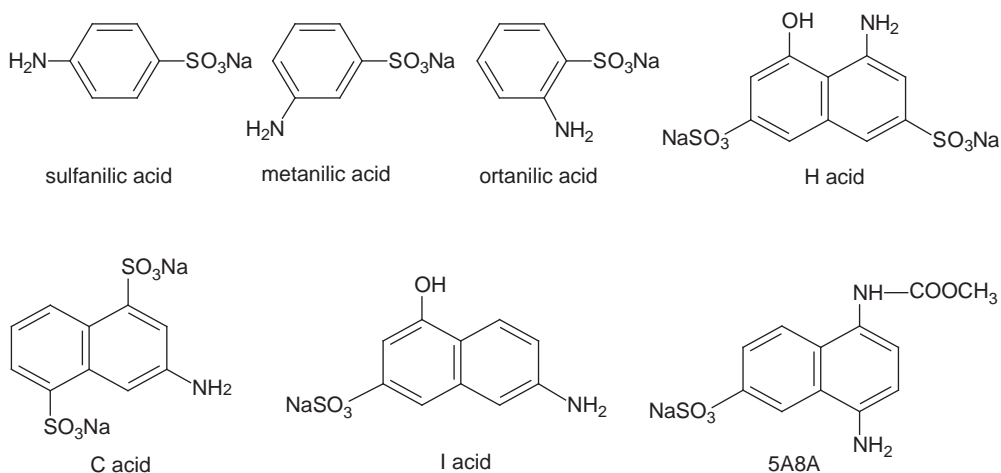


A number of natural compounds contain in their molecule amino and alcohol groups. One such example is sphingosine or 2-amino-4-octadecene-1,3-diol. Sphingosine is an important component of sphingolipids. Sphingosine pyrolysis generates a complex mixture of compounds.

### Compounds used as coupling agents in azo dyes

A number of amines are used in azo dyes industry, either as coupling agents or for the formation of diazo salts as a result of their reaction with HNO<sub>2</sub> (in acidic medium). These amines contain, besides

NH<sub>2</sub>, other functional groups such as OH, SO<sub>3</sub>H, SO<sub>3</sub>Na, etc. Some of these amines are shown below:



The main pyrolysis products, between 500 °C and 800 °C, of these compounds consist of aniline (for single cycle compounds), aminonaphthalene (for naphthalene derivatives) and sulfur dioxide, or sulfur. De-sulfonation seems to be the first step during pyrolysis. In the case of I acid, CO is also generated and the SO<sub>2</sub> formed in the first step is reduced to sulfur. Other compounds such as CO<sub>2</sub>, benzene, styrene, naphthalene, and char are also produced by pyrolysis [24]. Pyrolysis has also been used for the identification of aromatic amines generated from some azo dyes [25].

### Aromatic heterocyclic amines

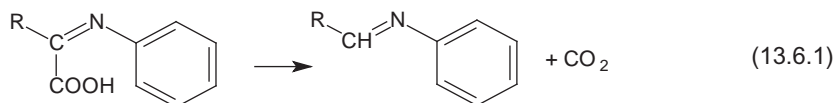
The amino group can be attached to an aromatic heterocyclic structure to form a heterocyclic amine. Pyrolysis results for various aromatic heterocyclic structures are presented in Chapter 21. Aromatic heterocyclic amines have a high stability to heating. For this reason, aromatic heterocyclic amines are formed during various thermal processes, such as pyrolysis of certain amino acids [26–31] (see Chapter 18). Some other heterocyclic amines are generated from proteins or from more complex chemical reactions involving sugars and nitrogenous compounds. Some heterocyclic amines of this type are discussed in Section 21.3. Pyrolysis of these compounds is likely to take place similar to that of aromatic amines (with a carbon atoms ring) and is influenced by other substituents on the molecule.

## 13.6. IMINES

### General aspects

Imines are compounds containing a carbon–nitrogen double bond  $\geq C=N-$  having substituents that can be the same or different at the carbon and nitrogen atoms. Imines typically result from the condensation reaction of a carbonyl compound and NH<sub>3</sub>, or an amine. The compounds formed with NH<sub>3</sub> are not stable, while those formed with amines, particularly when the substituent to the nitrogen is an aromatic ring, are stable and also known as Schiff bases. When the Schiff base is formed with an aromatic molecule such as aniline, the resulting compound is also known as an anil. Little information is available in the literature regarding thermal stability of Schiff bases. However, the compounds appear to be relatively stable to heating. For example, the anils of keto acids generate by pyrolysis a Schiff base eliminating CO<sub>2</sub>, which is an indication that the carboxyl group in the specified compound is less stable

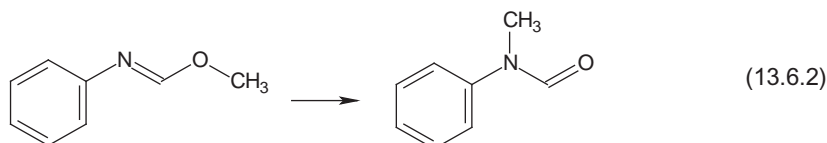
than the imine group [12]. The reaction is shown below:



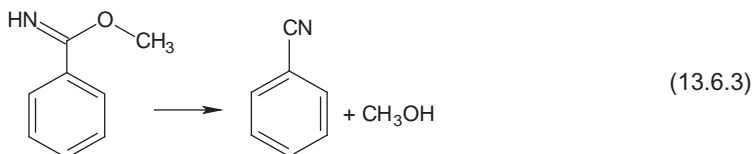
Phenylhydrazones also generate Schiff bases by decomposition, demonstrating once more that Schiff bases are more stable to heating than the parent hydrazone molecule.

Schiff bases form stable complexes with certain transitional metals such as  $\text{Cu}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{U(VI)}$ , etc. These complexes are typically stable to heating, and several reports describe their thermal decomposition [32–34].

An interesting rearrangement is seen in imino ethers (Chapman rearrangement, see Section 2.4). An imino ether is changed in this rearrangement into a substituted amide, as shown below for 2-aza-1-methoxy-2-phenylethane in a thermal decomposition that takes place at  $240^\circ\text{C}$  with heating for about 8 h:



The yield of *N*-methyl-*N*-benzamide in the pyrolysis of 2-aza-1-methoxy-2-phenylethane is only about 40%. Other similar imino ethers such as 2-aza-1-ethoxy-2-phenylethane and 2-aza-1-methoxy-1,2-diphenylethane show the same rearrangement. On the other hand, methoxy-phenylmethanimine does not show the same rearrangement and generates mainly methanol and benzonitrile in a reaction as shown below:



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## CHAPTER 14

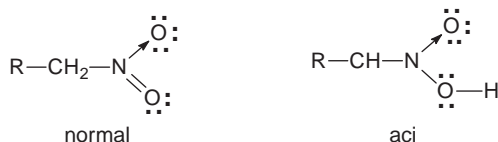
*Pyrolysis of Other Nitrogen Containing Compounds***14.1. NITRO AND NITROSO COMPOUNDS****General aspects**

Besides the amine functional group, which is common in numerous natural or synthetic compounds, a number of other nitrogen containing functional groups are known. The compounds with functional groups containing nitrogen are presented in this book in several separate chapters. Chapter 13 was dedicated to amines and imines. This present chapter includes compounds with functional groups that contain nitrogen but are not derivatives of organic acids. This class includes various compounds with groups such as nitro ( $-\text{NO}_2$ ), nitroso ( $-\text{NO}$ ), hydroxylamine ( $-\text{NHOH}$ ), oxyamine ( $>\text{N}-\text{O}-$ ), oxime ( $>\text{C}=\text{NOH}$ ), amine oxide ( $\equiv\text{N}\rightarrow\text{O}$ ), hydrazo ( $-\text{NH}-\text{NH}-$ ), diazo ( $-\text{N}=\text{N}-$ ), azoxy ( $-\text{N}=\text{N}(\text{O})-$ ), and azide ( $-\text{N}_3$ ). Compounds with other nitrogen containing functional groups that can be considered derivatives of organic acids are presented in Chapters 19 and 20.

The structure of  $\text{NO}_2$  is that of a free radical (the unpaired electron is not usually shown in the structure). The compound is assumed to have one of the two resonant forms:



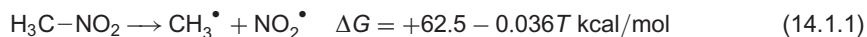
Nitroderivatives with the  $\text{NO}_2$  group connected to an aliphatic hydrocarbon chain may have two tautomeric forms, the “normal” and the “aci,” which are shown below:



In pyrolytic reactions, it can be assumed that only the normal form is involved, since the aci form is common only in basic media.

**Nitromethanes**

Nitromethane  $\text{CH}_3-\text{NO}_2$  and other nitro compounds are considered energetic materials (materials with a high amount of stored chemical energy that can be released). For this reason, nitromethane pyrolysis has been the subject of a large number of studies [1–16]. Several decomposition mechanisms are possible for nitromethane pyrolysis. One of these mechanisms begins with the C–N bond cleavage. The initiation reaction can be written as follows:



The  $\Delta H$  for reaction 14.1.1 is around 60 kcal/mol, but there is some disagreement in the literature regarding the precise value [7,15,17]. The kinetics of reaction 14.1.1 has been studied in various conditions. Shock wave pyrolysis experiments were performed on nitromethane in the concentration range 0.2%–1.5% diluted with argon or with nitrogen, in the temperature range 850 K–1550 K, and with pressures between 190 kPa and 900 kPa [2]. The experiments showed that the rate

constants for reaction 14.1.1 at low pressure depend on the diluent gas and have the following expressions:

$$k [\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}] = 10^{17.11} \exp \left[ \frac{-182.6 \text{ (kJ/mole)}}{RT} \right] \text{ (nitrogen diluted)} \quad (14.1.2)$$

$$k [\text{cm}^3 \text{ mole}^{-1} \text{ s}^{-1}] = 10^{17.574} \exp \left[ \frac{-207.0 \text{ (kJ/mole)}}{RT} \right] \text{ (argon diluted)} \quad (14.1.3)$$

The expression for the rate constant at high pressure is given by the expression:

$$k^\infty (\text{s}^{-1}) = 10^{16.2} \exp \left[ \frac{-247.0 \text{ (kJ/mole)}}{RT} \right] \quad (14.1.4)$$

Following the formation of  $\text{CH}_3^\bullet$  free radical and of  $\text{NO}_2$  in nitromethane pyrolysis, a number of propagation reactions occur. These reactions and their parameters  $A$  and  $E^\ddagger$  in Arrhenius equation are given in Table 14.1.1 [7]. Table 14.1.1 also gives the enthalpies  $\Delta H$  for the listed reactions. The reported values [7] were a compilation of literature data and some results obtained using for pyrolysis a static system in the temperature range 400–500 °C.

As seen from the reactions listed in Table 14.1.1, a number of small molecules are generated during  $\text{CH}_3\text{NO}_2$  pyrolysis. These reactions explain the pyrolysate composition, which includes as main components  $\text{NO}$ ,  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{NO}_2$ ,  $\text{HCN}$ , and  $\text{H}_2\text{O}$ . Other molecules present in the pyrolysate are  $\text{H}_2$  (from termination reaction between two  $\text{H}^\bullet$  radicals or by hydrogen abstraction),  $\text{HCHO}$ ,  $\text{CO}_2$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ ,  $\text{CH}_3\text{OH}$ ,  $\text{HCOOH}$  (from  $\text{HCOO}^\bullet$  radical),  $\text{C}_2\text{H}_4$  (from  $\text{CH}_3$  free radicals), etc.

A more detailed decomposition mechanism and the simulation of the process using a computer program was obtained using 99 model reactions [10]. Literature information is available regarding the bond energies for compounds with weak C–N bonds that may be involved in nitromethane pyrolysis [18]. Also, it has been shown that pyrolysis of nitromethane is a complex process, with many secondary reactions and competition between different channels that lead to a pyrolysate component [15]. Besides simple bond cleavage, the reactions during nitromethane pyrolysis involve rearrangements, molecular eliminations, etc. For example, the reverse reaction of the main decomposition process, i.e. recombination of  $\text{CH}_3^\bullet$  and  $\text{NO}_2^\bullet$ , may lead not only to  $\text{CH}_3\text{NO}_2$  but also to  $\text{CH}_3\text{ONO}$  (methyl nitrite). Methyl nitrite may further decompose adding new paths to the pyrolysis process by reactions as shown below:



However, theoretical work on nitro–nitrite rearrangement showed that this reaction should not play an important role in nitromethane decomposition [19]. Thermal decomposition of methyl nitrite and of *n*-propyl nitrite and *tert*-butyl nitrite were separately investigated, and the rate constants for these reactions were evaluated and reported in the literature [20].

Nitromethane decomposition on catalysts [7,11] as well as its oxidative pyrolysis and behavior in flames also were reported in the literature [2,11]. Nitromethane ignites in oxygen, and the kinetics of the ignition process (e.g. calculation of the ignition delay in different experimental conditions) is detailed in the literature [2].

Dinitromethane  $\text{CH}_2(\text{NO}_2)_2$  is much less stable to heating than nitromethane. However, the estimated bond energy for the C–N bond in dinitromethane is between 46.6 kcal/mol and 52.8 kcal/mol, and the decomposition is attributed to a mechanism different from the formation of free radicals.

TABLE 14.1.1. Reactions during pyrolysis of  $\text{CH}_3\text{NO}_2$ , their estimated parameters in Arrhenius equation  $k = A \exp(-E''/RT)$ , and the corresponding enthalpy [7–9]

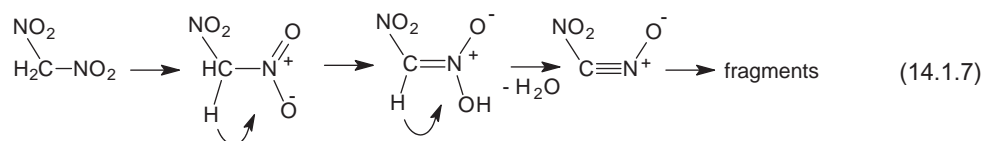
Reaction	$A^*$	$E^\ddagger$ (kcal/mol)	$\Delta H$ (kcal/mol)
$\text{CH}_3\text{NO}_2 \rightarrow \text{CH}_3^\bullet + \text{NO}_2^\bullet$	$6.62 \times 10^{14**}$	56.5**	+60.1
$\text{CH}_3^\bullet + \text{NO}_2^\bullet \rightarrow \text{CH}_3\text{NO}_2$	$5.0 \times 10^{11}$	0	–60.1
$\text{CH}_3^\bullet + \text{NO}_2^\bullet \rightarrow \text{CH}_3\text{O}^\bullet + \text{NO}^\bullet$	$10^{12}$	0	–17.1
$\text{CH}_3\text{NO}_2 + \text{CH}_3^\bullet \rightarrow \text{CH}_4 + \text{CH}_2\text{NO}_2^\bullet$	$2.4 \times 10^{11}$	9	–8
$\text{CH}_3\text{NO}_2 \rightarrow \text{CH}_3\text{O}^\bullet + \text{NO}^\bullet$	$10^{13}$	36	–30
$\text{CH}_3^\bullet + \text{NO}^\bullet \rightarrow \text{HCN}^\bullet + \text{H}_2\text{O}$	$3.0 \times 10^{13}$	4	–83.6
$\text{CH}_3\text{NO}_2 + \text{OH}^\bullet \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{NO}_2^\bullet$	$2.1 \times 10^{12}$	5	–23.3
$\text{CH}_3\text{O}^\bullet + \text{OH}^\bullet \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{O}$	$4.3 \times 10^{13}$	3	–32
$\text{CH}_3^\bullet + \text{NO}^\bullet \rightarrow \text{CH}_3\text{NO}$	$4.0 \times 10^{12}$	0	–39.9
$\text{CH}_2\text{NO}_2^\bullet + \text{CH}_2\text{O} \rightarrow \text{CH}_3\text{NO}_2 + \text{HCO}^\bullet$	$2.5 \times 10^{13}$	10	–8.9
$\text{HCO}^\bullet + \text{NO}_2^\bullet \rightarrow \text{CO} + \text{HNO}_2$	$10^{13}$	0	–61.6
$\text{HNO}_2 \rightarrow \text{OH}^\bullet + \text{NO}^\bullet$	$4.6 \times 10^{14}$	45	49.3
$\text{CH}_3\text{NO}_2 + \text{CH}_3\text{O}^\bullet \rightarrow \text{CH}_2\text{NO}_2^\bullet + \text{CH}_3\text{OH}$	$1.3 \times 10^{12}$	9	–7.5
$\text{CH}_3\text{O}^\bullet + \text{NO}^\bullet \rightarrow \text{CH}_2\text{O} + \text{HNO}$	$10^{11}$	0	–27.3
$\text{CH}_3\text{O}^\bullet + \text{NO}_2^\bullet \rightarrow \text{CH}_2\text{O} + \text{HNO}_2$	$5.0 \times 10^{12}$	0	–56.1
$\text{CH}_2\text{NO}_2^\bullet + \text{HNO}_2 \rightarrow \text{CH}_3\text{NO}_2 + \text{NO}_2^\bullet$	$10^{12}$	0	–17.7
$\text{HCO}^\bullet + \text{NO}_2^\bullet \rightarrow \text{HCO}_2^\bullet + \text{NO}^\bullet$	$3.1 \times 10^{13}$	4	–31.3
$\text{HCO}_2^\bullet + \text{NO}_2^\bullet \rightarrow \text{CO}_2 + \text{HNO}_2$	$3.5 \times 10^{13}$	4	–84.2
$2 \text{HNO} \rightarrow 2 \text{OH}^\bullet + \text{N}_2$	$8.0 \times 10^{11}$	0	–28.8
$\text{HCO}^\bullet + (\text{M}) \rightarrow \text{CO} + \text{H}^\bullet + (\text{M})$	$7.2 \times 10^{13}$	15	16.7
$\text{NO}_2^\bullet + \text{H}^\bullet \rightarrow \text{OH}^\bullet + \text{NO}^\bullet$	$1.2 \times 10^{14}$	0	–29
$\text{CH}_3\text{NO}_2 + \text{H}^\bullet \rightarrow \text{CH}_2\text{NO}_2^\bullet + \text{H}_2$	$7.5 \times 10^{12}$	10	–8.2
$\text{CH}_3\text{NO} \rightarrow \text{HCN} + \text{H}_2\text{O}$	$2.0 \times 10^{-1}$	0	–41.5
$\text{CH}_3\text{NO} \rightarrow \text{CH}_3^\bullet + \text{NO}^\bullet$	$7.0 \times 10^{13}$	38	39.9
$\text{NO}^\bullet + \text{OH}^\bullet \rightarrow \text{HNO}_2$	$2.0 \times 10^{13}$	3.5	–49.3
$\text{NO}_2^\bullet + \text{OH}^\bullet \rightarrow \text{HNO}_3$	$2.0 \times 10^{13}$	3.5	–49.9
$\text{CH}_4 + \text{OH}^\bullet \rightarrow \text{H}_2\text{O} + \text{CH}_3^\bullet$	$2.0 \times 10^{11}$	0	–9.9
$\text{CH}_3\text{O}^\bullet + \text{NO}^\bullet \rightarrow \text{CH}_3\text{ONO}$	$10^{13}$	0	–40.7
$\text{CH}_3\text{ONO} \rightarrow \text{CH}_3\text{O}^\bullet + \text{NO}^\bullet$	$8.0 \times 10^{12}$	36	40.7
$\text{H}_2 + \text{OH}^\bullet \rightarrow \text{H}_2\text{O} + \text{H}^\bullet$	$10^{12}$	0	–15

Note: Compounds in bold indicate the major pyrolysis constituents.

\*The units for  $A$  are either  $\text{s}^{-1}$  or  $\text{cm}^3/\text{mol}\cdot\text{s}$ .

\*\*The value for the constant  $k$  for the dissociation of  $\text{CH}_3\text{NO}_2$  calculated using the parameters  $A$  and  $E^\ddagger$  from Table 14.1.1 with data from [7–9] is smaller than the one predicted by rel. 14.1.4 based on more recent results [17].

One proposed path for dinitromethane decomposition can be written as follows [21]:

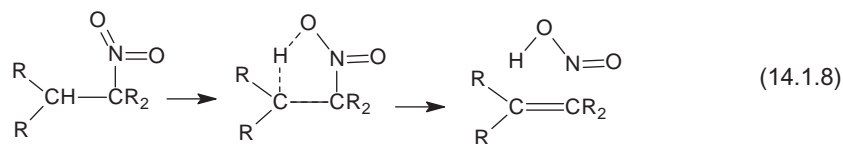


The fragments in reaction 14.1.7 consist of NO, CO,  $\text{N}_2$ ,  $\text{NO}_2$ , etc.



### Other nitroalkanes

Other nitroalkanes of short chain aliphatic hydrocarbons decompose mainly with the formation of NO, NO<sub>2</sub>, H<sub>2</sub>O, and an alkene. Lower levels of other compounds such as N<sub>2</sub> and HCN also are generated. Although the decomposition mechanism can be similar to that of nitromethane, which takes place mainly by a radicalic mechanism, the reaction of other nitroalkanes is assumed to take place mainly by a molecular concerted mechanism as shown below [19]:



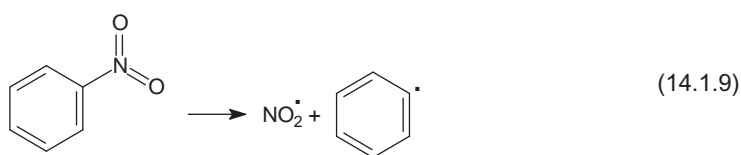
The formation of a double bond takes place in molecules such as nitroethane, nitropropane, etc. A triple bond is formed e.g. when nitroethylene is pyrolyzed, and the main pyrolysis products of nitroolefins with the NO<sub>2</sub> group connected to a sp<sup>2</sup> carbon lead to the formation of alkynes (for decomposition yields around 15%) [22,23].

Among other aliphatic nitro derivatives reported in the literature regarding pyrolysis are polynitro-adamantanes [24], phenylnitromethane [25], etc.

### Nitrobenzene

Nitrobenzene is stable to heating up to about 450 °C, the decomposition depending on heating time and also on the potential to have decomposition on surfaces (by heterogeneous reactions). The reaction products consist mainly of NO, NO<sub>2</sub>, benzene, biphenyl, aniline, dibenzofuran, and lower levels of naphthalene. The variation in the level of nitrobenzene left undecomposed in a flow-through pyrolyzer consisting of a stainless steel tube and a reactor with a residence time of 20 s is shown in Figure 14.1.1 [26].

An early decomposition mechanism assumed that NO<sub>2</sub> is generated from the C–N bond cleavage, followed by further reactions of phenyl radicals [27]. The reaction can be written as follows [28]:



The kinetics of this reaction is described by the following Arrhenius equation [29]:

$$k \text{ (s}^{-1}\text{)} = 10^{17} + \exp \left[ \frac{-69.0 \text{ (kcal/mol)}}{RT} \right] \quad (14.1.10)$$

The free phenyl radicals can further react to form biphenyl or can interact with other reaction participants by hydrogen transfer to form benzene. Other reaction products can also be explained by the initial formation of phenyl free radicals. The variation in the weight % (generated from area counts in the chromatographic separation) for the resulting compounds in nitrobenzene pyrolysis is given in Figure 14.1.2.

A different mechanism of nitrobenzene pyrolysis suggests the formation of nitrosobenzene as an intermediate product [26]. The C–N bond energy in nitrobenzene is about 62 kcal/mol, while the homolytic cleavage of phenyl nitrite into NO and phenoxy radicals is only 23.7 kcal/mol. For this reason, the isomerization of nitro group (NO<sub>2</sub>) into nitrite (ONO) followed by nitrite decomposition has been considered as a viable reaction path. However, the formation of phenoxy radicals would imply the

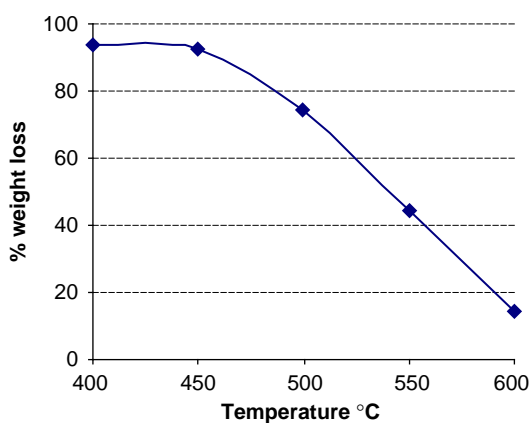


FIGURE 14.1.1. Level of nitrobenzene left undecomposed in a flow-through pyrolyzer at different temperatures (20 s residence time).

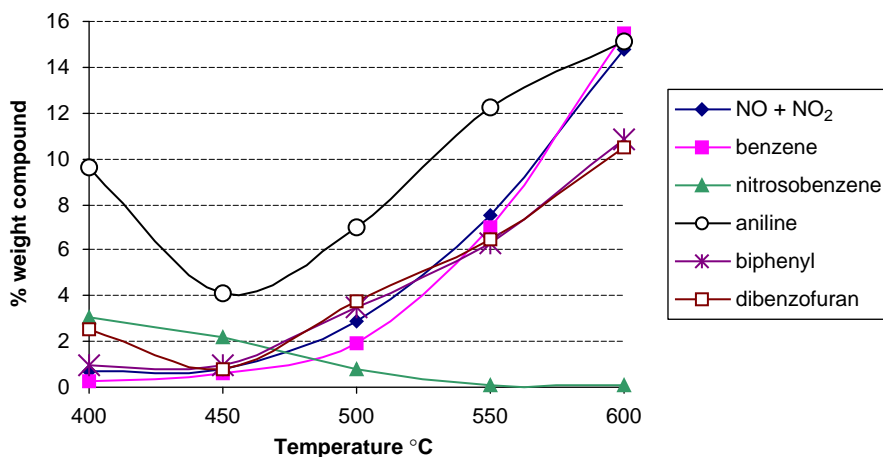


FIGURE 14.1.2. Level of various pyrolysis products during nitrobenzene pyrolysis in a flow-through pyrolyzer at different temperatures (20 s residence time) [26].

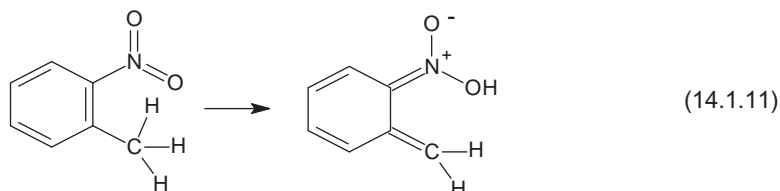
formation of a considerable level of phenol during nitrobenzene pyrolysis. Phenol was reported as present in the pyrolysate of nitrobenzene in some studies [27] and was not detected in other studies [26]. Different results generated by different studies regarding nitrobenzene pyrolysis were attributed to heterogeneous reactions influenced by the surfaces of the reactors used in different experiments [26]. The route with nitrosobenzene formation is supported by the finding that nitrosobenzene is detected in nitrobenzene pyrolysate, and its level decreases as the temperature increases (see Figure 14.1.2). The formation of a large proportion of benzene in nitrosobenzene pyrolysate supports the formation of phenyl radicals in the pyrolysis and not that of phenoxy radicals.

Pyrolysis of nitrobenzene has been studied also under the influence of catalysts [29] with the purpose of eliminating this compound from organic waste.

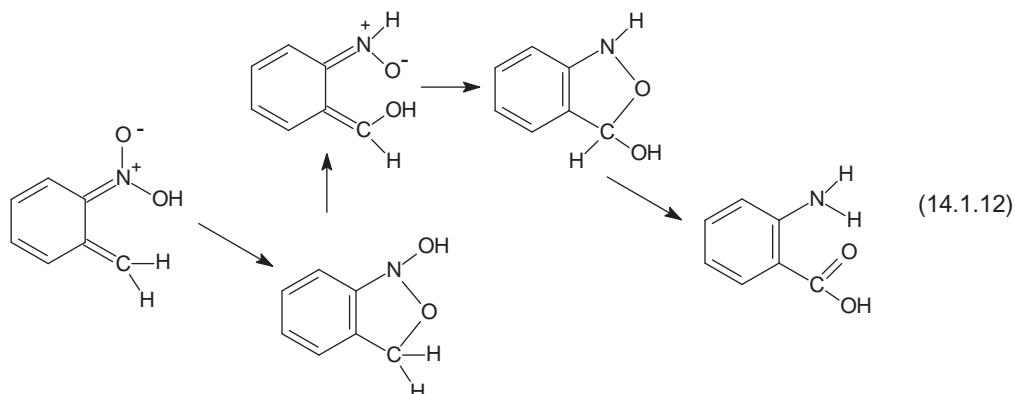
#### Other nitroaromatic derivatives

Various studies were reported in the literature regarding the thermal stability of nitrobenzenes with additional substituents on the phenyl ring [30–34]. Among these substituents is included the  $-\text{CH}_3$

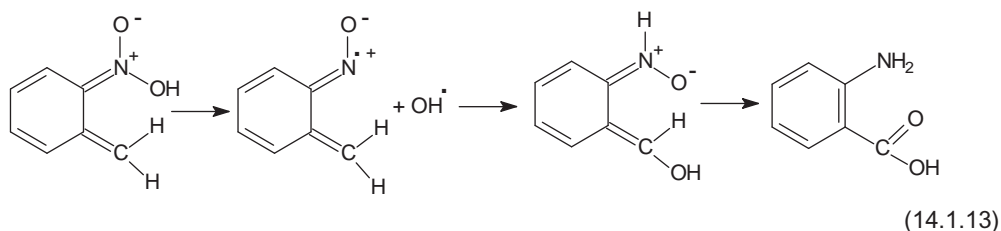
group [30,33–35]. This group affects the pyrolysis outcome such that the pyrolysis of *o*-nitrotoluene at 600 °C (0.05 mole *o*-nitrotoluene in 0.5 mole methanol at 600 °C with heating time 11 s) generates very low levels of expected toluene, or methylbiphenyl. The main reaction product in the presence of methanol is methyl anthranilate and in the absence of methanol is aniline. Various reaction mechanisms were proposed for explaining the reduction of NO<sub>2</sub> group to amine and the oxidation of the CH<sub>3</sub> group. These include the intramolecular hydrogen transport, the formation of nitrite in a nitro–nitrite rearrangement followed by the nitrite decomposition, and the radical detachment of the nitro group (similar to nitrobenzene case). The intramolecular hydrogen transport mechanism seems to be the most favored energetically for the first stage of thermal decomposition. This reaction can be written as follows:



The reaction can continue without involving the formation of free radicals, as shown below:



A different path may involve the formation of OH• free radicals generated by the cleavage of the N<sup>+</sup>–OH bond, which can continue the reaction with the end result as the formation of anthranilic acid in a reaction as follows:



The anthranilic acid further generates CO<sub>2</sub> and aniline. The Arrhenius equation for the formation of anthranilic acid from *o*-nitrotoluene is the following [29]:

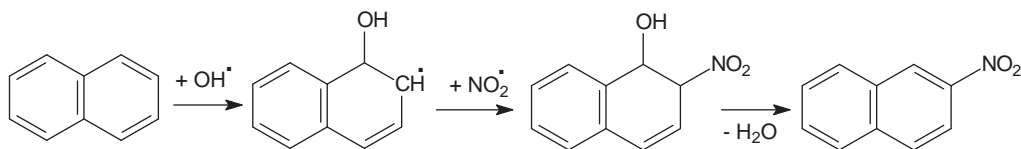
$$k \text{ (s}^{-1}\text{)} = 10^{12.4} + \exp \left[ \frac{-49.5 \text{ (kcal/mol)}}{RT} \right] \quad (14.1.14)$$

Other reaction mechanisms for the thermal decomposition of *o*-nitrotoluene are also possible.

Pyrolysis of dinitro derivatives of benzene (*o*-, *m*-, *p*-) is also reported in the literature [36,37]. The thermal decomposition takes place similar to that of nitrobenzene. Among the pyrolysis products are nitrobenzene, nitroaniline, and traces of benzofurazan and NO. The suggested reaction mechanisms involve either the cleavage of a C–N bond or nitro–nitrite isomerization followed by further decomposition of the nitrite.

Dinitro and trinitrotoluenes also were investigated regarding their pyrolysis [34,38]. By pyrolysis at 316 °C, some of the 2,4,6-trinitrotoluene remained undecomposed. The fragment molecules detected in the pyrolysate included 1,3,5-trinitrobenzene, 2,4,6-trinitrobenzyl alcohol, 2,4,6-trinitrobenzaldehyde, 2,4,6-trinitrobenzoic acid, 4,6-dinitro-2,1-benzisoxazole, and 4,6-dinitroanthranil. The decomposition mechanism is similar to that of nitrotoluene.

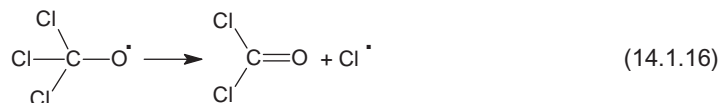
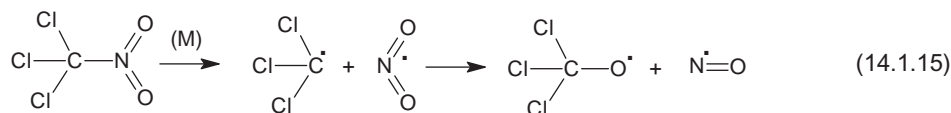
1-Nitronaphthalene is very stable to thermal degradation. Its decomposition products include naphthalene, 1-aminonaphthalene, dinitrotoluene, and char. 1,5-Dinitro-naphthalene is also very stable to thermal degradation and generates 1-nitro-naphthalene and traces of naphthalene. The high stability of nitronaphthalene (to temperatures higher than 700 °C) points out that nitro polyaromatic hydrocarbons are compounds stable to heating. For this reason, their formation in various combustion processes is of high concern. The formation of 2-nitronaphthalene, for example, is likely to take place in the burning processes where naphthalene, free OH<sup>•</sup> radicals, and NO<sub>2</sub> are present, by the following mechanism:



Since the resulting 2-nitronaphthalene is very stable to elevated temperatures, the compound is likely to be present in the gases resulting from the burning [39–41]. Among the nitro-PAHs identified in the environment are 1-nitropyrene, 2-nitropyrene, 3-nitrofluoranthene, 2-nitrofluoranthene, and 8-nitrofluoranthene. These compounds were identified in diesel exhaust or in soil.

### Nitroaromatic compounds with additional functionalities

A number of compounds containing NO<sub>2</sub> groups and, in addition, other functional groups were studied regarding their behavior during pyrolysis, and the results are reported in the literature. Some of these compounds are derived from aliphatic nitro compounds, such as trichloronitromethane (chloropicrin) CCl<sub>3</sub>–NO<sub>2</sub>. Thermal decomposition of chloropicrin has phosgene (COCl<sub>2</sub>) as the main decomposition product [42,43]. One study regarding chloropicrin pyrolysis [42] was performed in a static system in the temperature range 100–530 °C, at the initial pressures of the parent molecule at 25 Torr, and 10–120 min heating time. The reaction progresses as shown below:

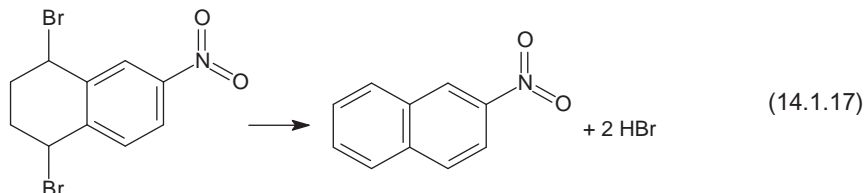


The free radicals Cl<sup>•</sup> may generate Cl<sub>2</sub> by termination reactions or may continue to participate in other propagation reactions. The formation of other pyrolysis products including NO and Cl<sub>2</sub> are explained also by reactions 14.1.15 and 14.1.16. Besides these compounds, lower levels of CO and CCl<sub>4</sub> are formed in the reaction.

The pyrolysis of diphosgene (CCl<sub>3</sub>–O–COCl) occurs similar to chloropicrin. This compound decomposes to generate COCl<sub>2</sub>, CCl<sub>4</sub>, CO, and Cl<sub>2</sub>.

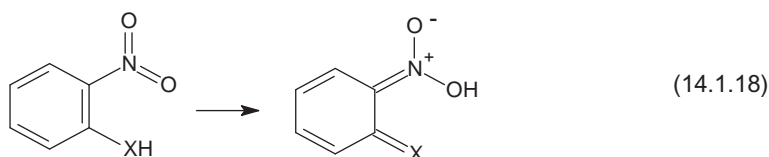
Pyrolysis of 1-(hydroxyimino)-3-nitro-1,2,3-triphenylpropane also was reported in the literature [44]. The pyrolysate obtained at temperatures up to 375 °C of this compound contains 2,3,5-triphenylpyrrole (15%–19%), low levels of benzonitrile (0.5%–1.5%), undecomposed initial product, and tar.

Other nitro compounds with additional functional groups are from the aromatic series. For example, the effect of groups such as COOH, NH<sub>2</sub>, OH, F, Cl, Br, I, etc. on the thermal decomposition of nitro aromatic compounds has been reported in the literature [32–34,39,45]. Pyrolysis of these compounds depends on the nature of the substituent, and may occur first at the nitro group or first at the additional functional group. An interesting reaction is given, for example, by 1,4-dibromo-6-nitro-1,2,3,4-tetrahydronaphthalene, which generates by pyrolysis 2-nitronaphthalene:



On the other hand, *p*-iodonitrobenzene decomposes similar to nitrobenzene, the iodine substituent remaining mostly not affected [34].

The lack of participation in the pyrolytic reactions of functional groups such as F or Cl also is seen when these functional groups are present in the nitrotoluene molecule. Pyrolysis in these cases takes place with the formation of chloro or fluoroanthranilic acid, which further may lose CO<sub>2</sub> by decarboxylation [33]. In the absence of CH<sub>3</sub> groups and in the presence of substituents containing hydrogen (except COOH), the initiation reaction for compounds having a functionality in the *ortho* position to a nitro group proceeds similarly to reaction 14.1.11, as shown below:

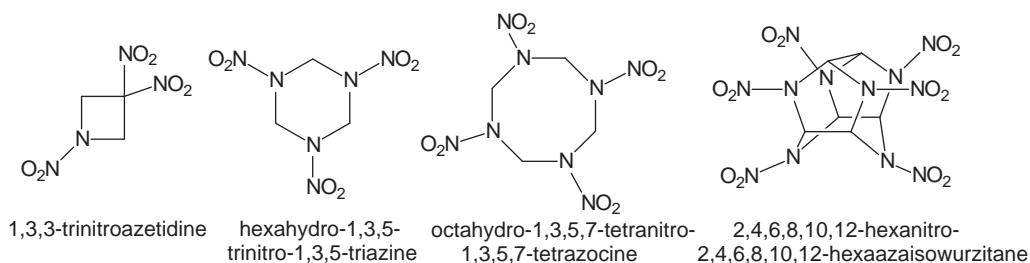


The reaction continues with the result of further oxidation, if possible, of the X group.

Pyrolysis of some other more complex molecules containing nitro groups also was reported in the literature [46].

### Nitro derivatives of heterocycles

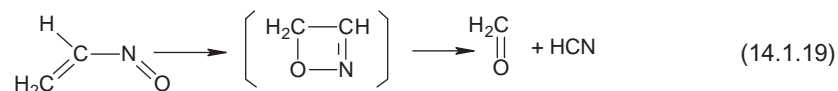
Heterocyclic compounds with the NO<sub>2</sub> group directly connected to the nitrogen are known compounds, some of these being used as energetic materials (explosives). The formulas of several such compounds are shown below:



Because of the utility of these compounds as explosives, several studies on their stability were reported in the literature [47–49]. Other studies on thermal decomposition of nitro derivatives of heterocycles are reported [50].

### Nitroso compounds

There is only very limited information in the literature regarding nitrosoalkanes pyrolysis (this include pyrolysis of 2-nitrosopropene [51] and of nitrosoethylene [52]). Nitrosoethylene generates by heating HCHO and HCN in a reaction as shown below:



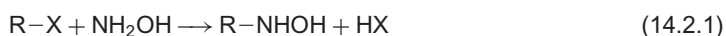
Pyrolysis of nitrosobenzene as a parent molecule begins around 275 °C with the formation of CO<sub>2</sub>, NO (3.4% area count in the pyrogram), benzene (62.9%), aniline+phenol (3.1%), undecomposed nitrosobenzene (8.4%), nitrobenzene (1.9%), naphthalene (trace), biphenyl (6.7%), dibenzofuran (1.7%), 2-phenylphenol (3.9%), and other (8%) [26].

Pyrolysis of nitrosophenols and nitrosonaphthols also was reported in the literature [53]. 4-Nitrosophenol, for example, generates by flash pyrolysis at 700 °C and 0.02 Torr, pyridine (20%), phenol (30%), and 4-aminophenol (5%) (relative to the parent compound). By pyrolysis in the same conditions as 4-nitrosophenol, 1-nitroso-2-naphthol and 2-nitroso-1-naphthol generate quinoline, isoquinoline, indene, and 2- or 1-naphthol (respectively).

## 14.2. HYDROXYLAMINES, OXYAMINES, AND *N*-ALKOXYAMMONIUM HYDROXIDE DERIVATIVES

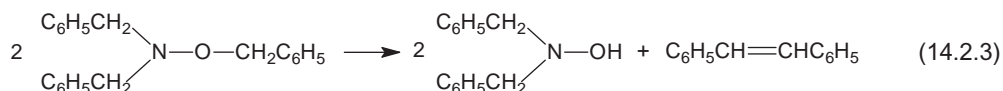
### General aspects

Hydroxylamine has the formula NH<sub>2</sub>OH, and the hydrogen's from the oxygen atom, from the nitrogen atom, or both can be replaced with organic radicals. The replacement can be practically achieved in reactions as shown below:



The compounds with the hydrogen from the nitrogen replaced with organic radicals are indicated as substituted hydroxylamines, and those with the general formula NH<sub>2</sub>O-R are known as oxyamines. Hydroxylamine reacts with aldehydes and ketones to form oximes, which are further discussed in Section 14.3. The reaction of NH<sub>2</sub>OH with organic acid esters leads to hydroxamic acids (see Chapter 20).

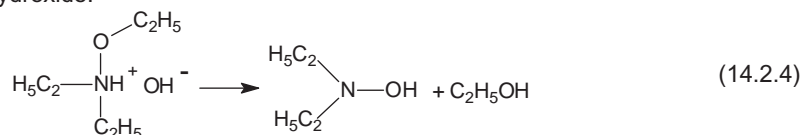
Several studies were performed on the pyrolysis of hydroxylamine itself and on various salts of hydroxylamine (which has a basic character) [54–56]. Among the few substituted hydroxylamines evaluated regarding thermal stability is tribenzyl hydroxylamine. This compound is not very stable to heating and during distillation under vacuum undergoes the following reaction [55]:



The decomposition of O-(2-nitrobenzyl)hydroxylamine hydrochloride or 1-[(aminooxy)methyl]-2-nitrobenzene hydrochloride also takes place before melting.

Related to hydroxylamines are *N*-alkyl-*N*-alkoxyammonium hydroxide derivatives. These compounds decompose upon heating with the formation of substituted hydroxylamines, as shown below for

diethylethoxyammonium hydroxide:



When no hydrogen is available on the nitrogen atom, *N*-methoxytrimethylammonium hydroxide generates trimethylamine, formaldehyde, and water. The isomeric compound, the methoxide of trimethylammonium hydroxide, generates by thermal decomposition trimethylamine oxide and methanol [55].

### 14.3. OXIMES AND OXIME DERIVATIVES

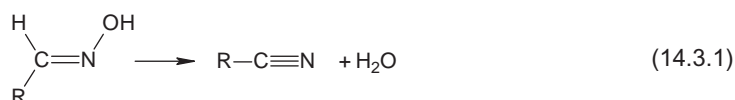
#### General aspects

The general formula of oximes is  $\text{R}_2\text{C}=\text{NOH}$ , the two R substituents being hydrogen or organic radicals (the same or different). Oximes can be generated from aldehydes or ketones by reaction with hydroxylamine and are frequently considered derivatives of aldehydes or ketones. For this reason, the names of oximes are typically derived from that of the related aldehyde or ketone with the addition of *oxime* (e.g. acetone oxime). The oximes generated from aldehydes are known as aldoximes, and those from ketones as ketoximes. Oximes show stereoisomerism *syn* and *anti*, since there is no free rotation around the double bond  $\text{C}=\text{N}$ .

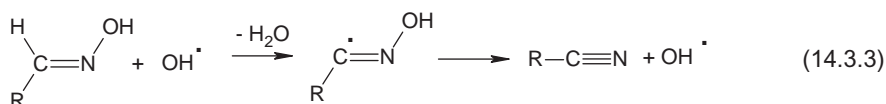
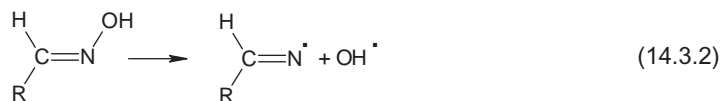
Oximes are able to form many derivatives. With strong acids such as HCl, they act as a base and form salts of the form  $\text{R}_2\text{C}=\text{NOH} \cdot \text{HCl}$  (in dry media). With strong bases such as NaOH, they act as acids and form salts of the form  $[\text{R}_2\text{C}=\text{NO}]^-\text{Na}^+$ . Also, the hydrogen from the  $=\text{NOH}$  group can be replaced with hydrocarbon radicals to form oxime ethers, and with acyl radicals to form oxime esters.

#### Oximes

Pyrolysis of aldoximes typically leads to a complex pyrolysate, although the main reaction is usually the formation of nitriles by water elimination. This reaction is shown as follows:

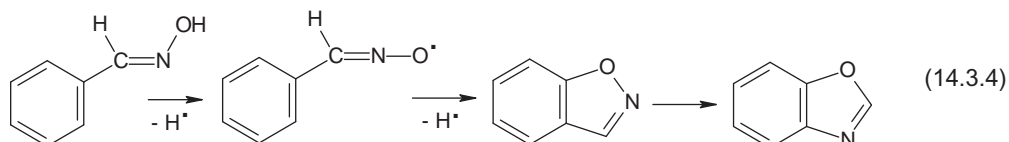


Formaldoxime generates, indeed, mainly HCN and  $\text{H}_2\text{O}$ . Acetaldehyde oxime (acetaldoxime) generates by pyrolysis in the temperature range 330–440 °C not only methylcyanide (ethanenitrile) and water but also forms some acetaldehyde,  $\text{N}_2$ , etc. [57]. The main reaction in these molecules takes place with a free radical mechanism by the cleavage of the N–OH bond and formation of  $\text{OH}^\bullet$  free radicals. These radicals further abstract H atoms connected to the carbon atom from other oxime molecules in a propagation reaction to form water. The nitriles are generated by further  $\text{OH}^\bullet$  elimination, and this reaction sequence is shown below:

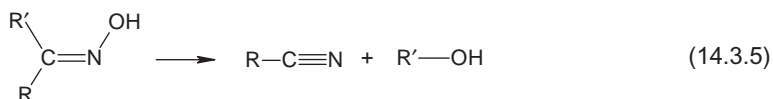


The rate constant  $k$  for the reaction  $\text{OH}^\bullet + \text{CH}_2\text{NOH} \rightarrow \text{H}_2\text{O} + \text{CH}^\bullet\text{NOH}$  was estimated at  $300^\circ\text{C}$   $k = 3.8 \times 10^{+8}$ , and for the reaction  $\text{OH}^\bullet + \text{CH}_3\text{CHNOH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{C}^\bullet\text{NOH}$  and the same temperature was estimated  $k = 1.3 \times 10^{+9}$  [58]. The free radicals  $\text{R}-\text{CH}=\text{N}^\bullet$  were found less reactive than  $\text{OH}^\bullet$  free radicals. Pyrolysis of formaldoxime and acetaldoxime was studied also in the presence of  $\text{NO}$  [57–59]. Similar results regarding pyrolysis, with the generation of the corresponding nitrile, were obtained for propionaldehyde oxime [60,61].

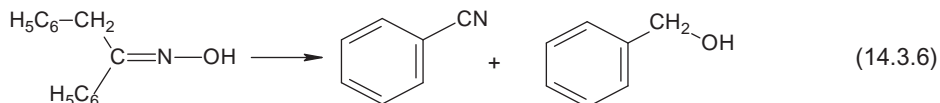
Reaction 14.3.1 is also the main decomposition route for some aromatic aldoximes. For example, benzaldoxime generates in flash vacuum pyrolysis (FVP) benzonitrile and benzoxazole. The reaction mechanism in this case seems to be the formation of iminoxyl radicals with the cleavage of the  $\text{O}-\text{H}$  bond rather than the cleavage of  $\text{N}-\text{OH}$  bond. The reaction of formation of benzoxazole from benzaldoxime is shown below [62]:



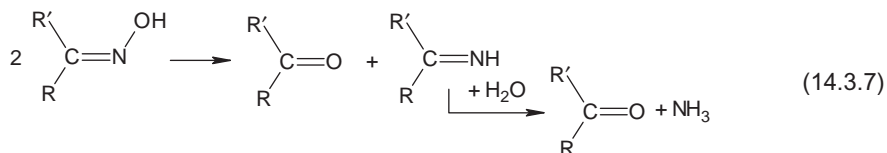
Pyrolysis of ketoximes can proceed similarly to that of aldoximes, the reaction occurring with the formation of a nitrile and an alcohol instead of water, as shown in the following reaction:



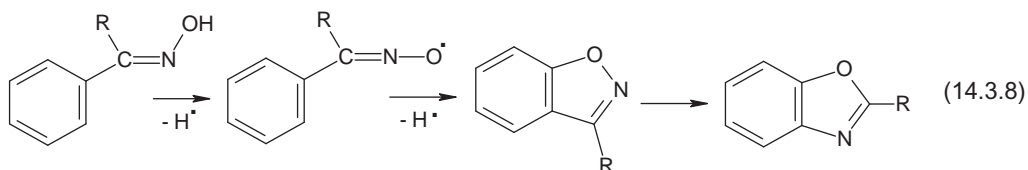
This is basically the reaction followed by phenyl benzyl ketoxime, which explodes at  $270^\circ\text{C}$  to form benzonitrile and benzyl alcohol as shown below:



The mechanism of this reaction is very likely similar to that of reaction 14.3.2, with the formation of  $\text{OH}^\bullet$  free radicals. Besides the compounds shown in reaction 14.3.6, the pyrolysate of phenyl benzyl ketoxime contains  $\text{NH}_3$ , 2,4,5-triphenyl-1H-imidazole and 2-phenylacetophenone. The formation of ammonia and of the ketone can be explained by the presence of small quantities of water formed during pyrolysis from secondary reactions such as the alcohol decomposition. When water is present, the reaction of ketoximes may occur as shown below:

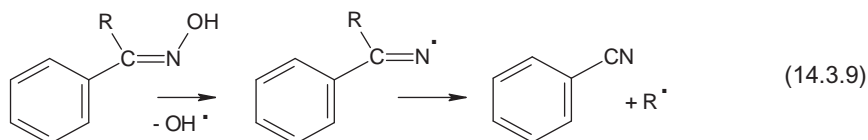


Ketoximes can also form benzoxazoles by pyrolysis. The formation of benzoxazoles is similar to reaction 14.3.4 and is shown below:



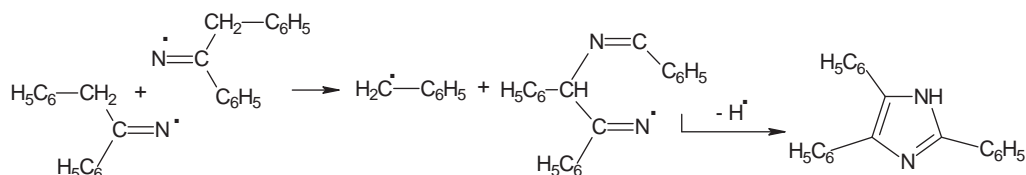


The formation of  $\text{OH}^\bullet$  free radicals is possible in ketoxime pyrolysis, and the reaction takes place as shown below:



The formation of  $\text{R}^1\text{R}^2\text{C}=\text{N}^\bullet$  iminyl free radicals accounts for various further reactions. These radicals can decompose to generate either  $\text{R}^1\text{CN}$  and  $\text{R}^{2\bullet}$  or  $\text{R}^2\text{CN}$  and  $\text{R}^{1\bullet}$ . The free radicals  $\text{R}^\bullet$  are responsible for the presence of hydrocarbons in oximes pyrolysates, including that of aromatic hydrocarbons.

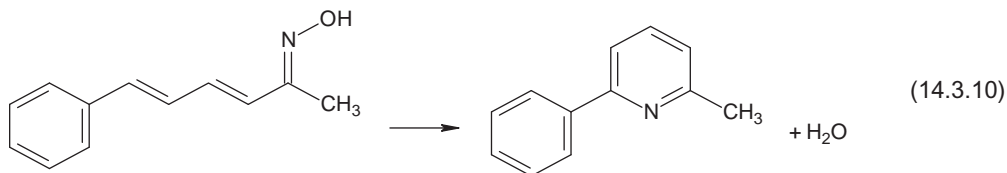
The same iminyl  $\text{R}^1\text{R}^2\text{C}=\text{N}^\bullet$  free radicals account for the formation of imidazoles in some oxime pyrolysis, by reactions shown below for phenyl benzyl ketoxime:



The formation in reaction 14.3.9 of  $\text{R}^\bullet$  free radicals (and with a lower probability of  $\text{C}_6\text{H}_6^\bullet$  free radicals and  $\text{RCN}$ ) explains the numerous side reactions noticed in oxime pyrolysis. One such example is given by the pyrolysis of acetone oxime (the simplest ketoxime), which takes place around  $270^\circ\text{C}$  and generates  $\text{CH}_4$ ,  $\text{NH}_3$ , and other small molecules.

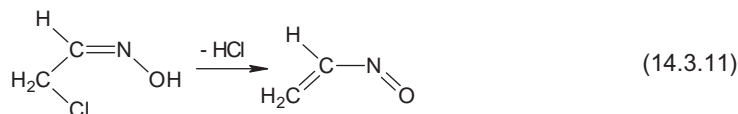
Pyrolysis of benzophenone oxime at  $800^\circ\text{C}$  [63] leads to the formation of expected benzonitrile, and in addition of benzophenone, benzophenone imine (following reaction 14.3.7), and also biphenyl, benzene, and 2-phenylbenzoxazole.

Other oximes generate products influenced by the structure of the whole molecule. For example, pyrolysis of 6-phenylhexa-3,5-dien-2-one oxime generates by pyrolysis 6-methyl-2-phenylpyridine as shown below:



Pyrolysis of more complex oximes was reported in the literature [53,63,64]. For example, pyrolysis of 5H-dibenzo[a,d]cyclohepten-5-one oxime and of 10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-one oxime was reported for a flow system working at 1.33 mbar and  $650^\circ\text{C}$  [63]. The pyrolysis products of 5H-dibenzo[a,d]cyclohepten-5-one oxime were 1-cyano-phenanthrene, 3H-[3,4-a,5]isoxazolodibenzo[b,f]cycloheptene, dibenzosuberone, dibenzosuberone imine, anthracene, and phenanthrene. In the pyrolysis of 10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-one oxime were generated 1-cyano-9,10-dihydrophenanthrene, 4-cyano-9,10-dihydrophenanthrene, 3H-[3,4-a,5]isoxazolo-9,10-dihydrodibenzo[b,f]cycloheptene, dibenzosuberone and dibenzosuberone imine, anthracene, phenanthrene, 1-cyano-phenanthrene, and 3H-[3,4-a,5]isoxazolodibenzo[b,f]cycloheptene. Although the resulting compounds in these pyrolytic reactions were rather complex, the formation of ketone imines and of corresponding ketones was the general reaction route (also proved for isodibenzosuberone oxime). Surface catalysis was considered as a favoring factor for these reactions.

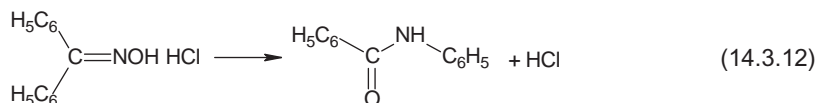
Pyrolysis of oximes containing additional functionalities may progress as expected involving only the oxime functionality or may be affected by the presence of the additional functionality. For example, pyrolysis of  $\text{ClCH}_2\text{CH}=\text{NOH}$  [65] generates nitrosoethylene, by the reaction shown below:



Further decomposition of nitrosoethylene following reaction (14.1.8) leads to the formation of HCN and formaldehyde.

In another example, pyrolysis of benzoin oxime (2-hydroxy-1,2-diphenylethane-1-one oxime) generates benzonitrile, benzaldehyde, and 2,4,5-triphenyl-1H-imidazole in reactions similar to those for phenyl benzyl ketoxime.

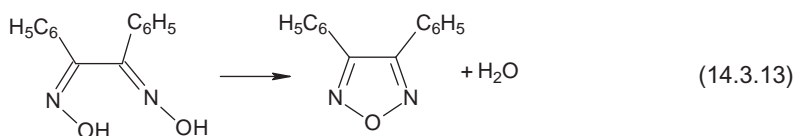
Pyrolysis of oxime hydrochloride was reported for benzophenone oxime HCl [55]. The thermal decomposition takes place with the formation of benzanilide (phenyl-*N*-benzamide) in a reaction similar to Beckmann transposition (see Section 2.4), as shown below:



The sodium salt of acetophenone oxime decomposes differently, forming benzonitrile (~15%),  $\text{NH}_3$  (~48%), benzoic acid (~37%), and traces of acetophenone, etc.

### Oximes of diketones

Three forms of oximes generated by  $\alpha$ -diketones are known and are indicated as  $\alpha$  or *anti*,  $\beta$  or *syn*, and  $\gamma$  or *amfi*. Pyrolysis of these isomeric compounds of the same diketone may lead to different results. For example, 1,2-diphenylethane-1,2-dione  $\gamma$ -oxime by heating at 155 °C eliminates  $\text{H}_2\text{O}$  and forms a 3,4-diphenyl-1,2,5-oxadiazole (3,4-diphenyl furazan):



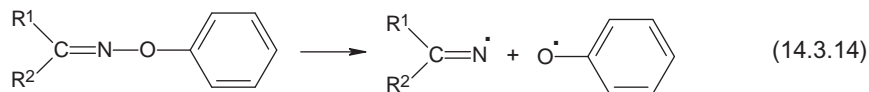
The  $\alpha$  and  $\beta$  isomers of the same oxime do not form the oxadiazole. The  $\alpha$  form suffers an isomerization into the  $\beta$ -form upon heating. The  $\beta$ -form, which is more stable to heating, forms a mixture of fragments when heated at higher temperatures.

Some oximes, such as dimethylglyoxime (butane-2,3-dione dioxime) form stable complexes with transition metal ions such as  $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Pd}^{+2}$  [66]. Thermal decomposition of these complexes with the formation of metal oxides has been studied and reported in the literature [66–68].

### Oximes ethers and esters

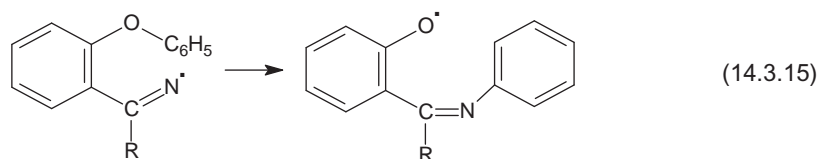
The replacement of the hydrogen atom from the  $=\text{NOH}$  group with a hydrocarbon radical leads to the formation of oxime ethers. The synthesis of oxime ether typically starts with a ketone and an oxyamine (O-substituted hydroxylamine). Thermal decomposition of several O-benzyl substituted ketoximes [69] showed that these compounds are not very stable to heating. The decomposition was performed in solvents such as tetraline, 9,10-dihydrophenanthrene, or 9,10-dihydroanthracene. The studied oxime ethers included seven dialkyl, two alkyl aryl, and two diaryl ketoximes O-benzyl ethers. During thermal

decomposition, compounds resulting from both the cleavage of the NO—C bond and from the cleavage of N—O bond were obtained. In a different study [70], the thermal decomposition of O-phenyl ketoxime ethers of six ketoximes were studied. In this case, thermal decomposition led to the cleavage of the N—O bond almost exclusively, with the formation of iminyl and phenoxy radicals:

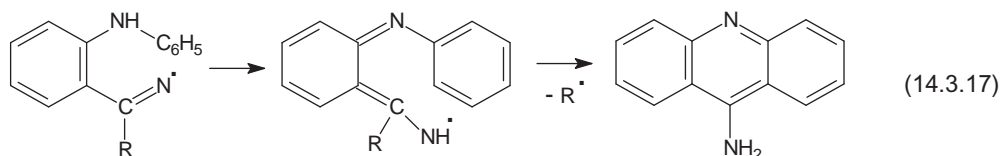
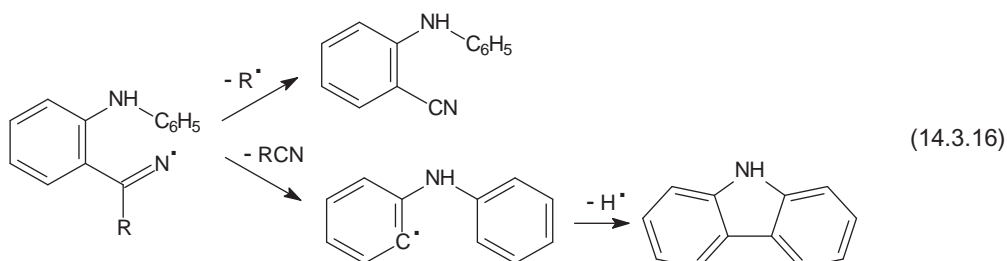


Further reactions observed for these free radicals are those that can be expected. The iminyl radical leads to the formation of a nitrile R<sup>1</sup> or R<sup>2</sup> free radicals. Condensations with the formation of oxazoles also were noticed.

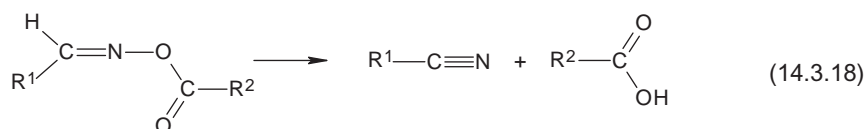
Depending on the general structure of the molecule, the iminyl radicals formed in reaction 14.3.14 can undergo a radical migration as shown below for a compound containing an additional ether group in the molecule [71]:



It is also possible that the migration does not take place, and further reactions may lead to the formation of heterocycles, as shown in the following reactions which take place when an additional amine group is present in the molecule [72,73]:

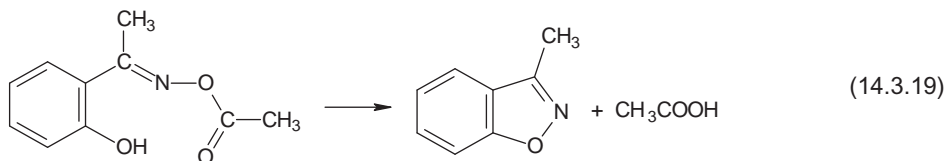


Pyrolysis of oxime esters was also reported in the literature [55,74]. Being a derivative of acids, oxime esters could have been included in Chapter 20, but since the oxime group is more important for the chemical properties of these compounds, they were classified together with oximes. The typical pyrolysis reaction in the case of aldoxime esters takes place at relatively low temperatures, around 150 °C, and proceeds with the formation of an acid, and a nitrile as shown below:



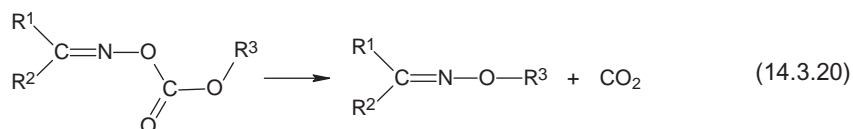
The reaction was verified for *O,N*-diacetyl-*o*-aminobenzaldoxime, monoacetyl-3,5-dibromosalicylal-doxime, etc.

In the case of ketoxime esters, thermal decomposition was evaluated for 2-hydroxy-acetophenone acetyl oxime, and the reaction leads to the formation of 2-methyl-1,2-benzisoxazole, as shown below:

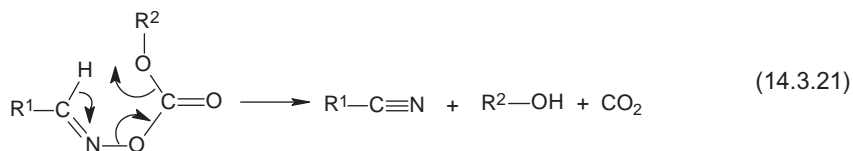


Pyrolysis of other ketoxime esters, such as those derived from cyclopentanone and cyclohexanone, was reported in the literature [74].

Another group of oxime derivatives are the carbonates. These compounds are typically obtained from oximes and chloroformates ( $\text{R}-\text{O}-\text{C}(\text{O})-\text{Cl}$ ). The resulting carbonates of ketoximes decompose at temperatures around  $200^\circ\text{C}$  with  $\text{CO}_2$  elimination, as shown in the reaction below:

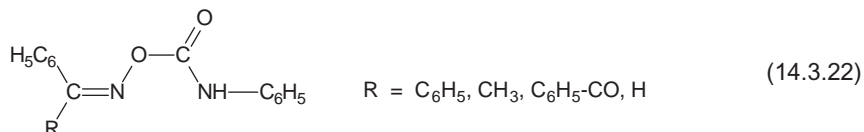


The reaction was verified for compounds with the R groups aryl (phenyl and *p*-substituted phenyl groups) [75]. In case of aldoxime carbonates, the resulting O-substituted oxime that would be generated by a reaction similar to 14.3.20 cannot be isolated and forms a nitrile and an alcohol. The reaction is shown below:

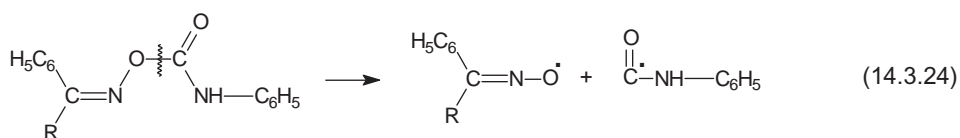
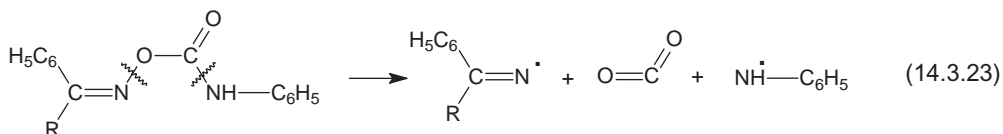


This reaction was verified for several oximes such as *anti-p*-nitrobenzaloxime, *syn-p*-chlorobenzaloxime, *syn*-benzaloxime, *syn-p*-methylbenzaloxime, and *syn-p*-methoxybenzaloxime [76].

Similar in structure with oxime carbonates are the substituted carbamoyl oxime derivatives. Pyrolysis of several compounds from this class has been reported in the literature [77]. The formulas for the compounds evaluated [77] are shown below:

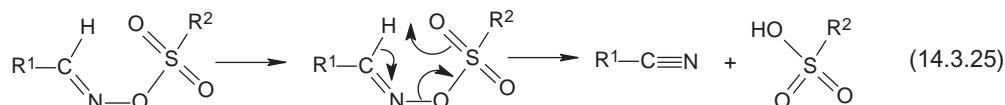


Thermal decomposition of these compounds takes place around  $220^\circ\text{C}$  and proceeds with two types of bond cleavage, as follows:



The multitude of free radicals formed in reactions 14.3.23 and 14.3.24 leads to the formation of a complex pyrolysate. For example, *O*-phenylcarbamoyl derivative of benzophenone oxime ( $R = C_6H_5$  in formulas 14.3.22) generates: benzene (trace), biphenyl (4%), aniline (14%), azobenzene (4%), 1,3-diphenylcarbamide (carbanilide) (5.5%), ketones (16%), nitriles (8%), aniline amides (anilides) (11.5%), oxazoles (14.7%), imines (13.3%), and some unchanged parent compound (4%). The iminyl radicals that further decompose are responsible for the formation of  $R^\bullet$  free radicals that lead to the formation of hydrocarbons such as benzene and biphenyl in the case of *O*-phenylcarbamoyl derivative of benzophenone oxime.

Sulfonyl oximes are also derivatives for which pyrolysis has been reported in the literature [78]. Decomposition of these compounds takes place by the following reaction:



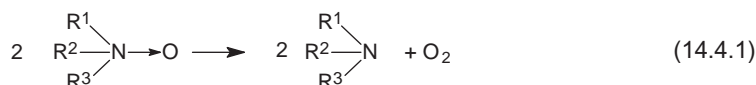
The reaction has been verified for  $R^1 = C_6H_5$ ,  $p\text{-CH}_3\text{O}-C_6H_4$ ,  $p\text{-CH}_3-C_6H_4$ ,  $p\text{-Cl}-C_6H_4$ ,  $p\text{-NO}_2-C_6H_5$ , and for  $R^2 = p\text{-CH}_3-C_6H_4$  (oxime tosylates).

Some kinetic parameters were reported for these oxime derivatives decompositions [79].

#### 14.4. AMINE N-OXIDES AND NITRONES

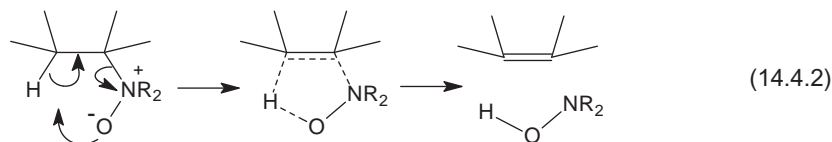
##### Amine N-oxides

Amine N-oxides are compounds with the general formula  $R_3N \rightarrow O$  or  $R_3N^+O^-$  where the R radicals can be the same or different and where between the nitrogen and the oxygen atoms is a coordinate covalent bond sometimes indicated as " $\rightarrow$ ." Thermal decomposition of these compounds occurs at mild heating at temperatures around 150 °C or even lower and can take place by two different reactions, one with the formation of oxygen and a tertiary amine and the other with the formation of a hydroxylamine and an alkene. The reaction with the elimination of oxygen and the formation of a tertiary amine is shown below:

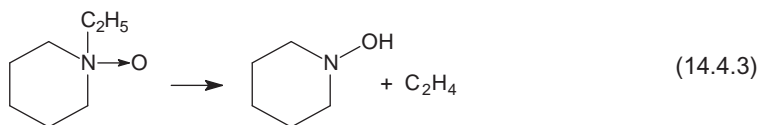


Examples of compounds that decompose by this reaction are dimethylaniline oxide, *N*-methylpiperidine oxide [55], dimethyllaurylamine oxide [80], and *N*-methylmorpholine-*N*-oxide [81]. These compounds generate by heating the corresponding free tertiary amine.

The other possible reaction is the formation of a hydroxylamine and an alkene. This reaction takes place by a concerted mechanism as follows:



As an example, ethylpiperidine oxide decomposes by this type of mechanism, the reaction being shown as follows:

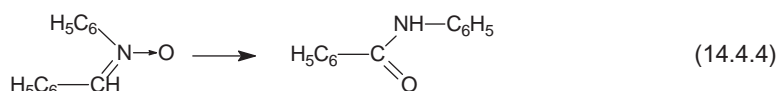


The same reaction is followed, for example, by tripropylamine oxide, which generates by heating *N*-dipropyl-hydroxylamine and propene. Even in the case of dimethyllaurylamine oxide, some 1-dodecene

is formed [80], showing that both reactions can occur for a given compound [82]. Other studies on thermal stability and decomposition of N-oxides (including N-oxides of some nitrogenous heterocycles) are reported in the literature [83].

### Nitrones

Nitrones are N-oxides of imines. Thermal decomposition of these compounds takes place at relatively low temperatures 120 °C–220 °C and can take different paths. Phenyl-*N*-phenyl nitrone decomposes around 120 °C to form benzanilide (phenyl-*N*-benzamide) as shown below:



In addition to the main reaction, several side reactions occur. When no hydrogen is connected to the carbon involved in the nitron molecule, reaction 14.4.4 cannot occur. A mixture of compounds is typically found in the pyrolysate, including the compound resulting from oxygen elimination in a reaction similar to 14.4.1 for amine oxides.

## 14.5. HYDRAZINES AND HYDRAZONES

### General aspects

Similar to the case of ammonia, which can generate amines, hydrazine ( $\text{H}_2\text{N}-\text{NH}_2$ ) has the capability to generate substituted hydrazines by the replacement of one or more hydrogen atoms with alkyl or aryl radicals. Similar to  $\text{NH}_3$  and to amines, hydrazines have a basic character and can form salts with the acids. When one nitrogen atom in the hydrazine molecule has a double bond to a carbon atom, the resulting compound is a hydrazone. Hydrazone molecules contain the group  $>\text{C}=\text{N}-\text{N}<$  where both the carbon and the nitrogen are connected with hydrogen, alkyl, or aryl radicals.

### Hydrazines

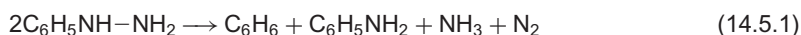
Pyrolysis of hydrazine has been the subject of several studies because the compound can be used as rocket fuel (see e.g. [84]). Pyrolysis of methylhydrazine, 1,1-dimethylhydrazine, and 1,2-dimethylhydrazine also was evaluated at very low pressure in the temperature range 650–1000 °C [85,86]. The decomposition of  $\text{CH}_3\text{NHNH}_2$  proceeds with the formation of  $\text{NH}_3$ ,  $\text{H}_2$ ,  $(\text{CH}_3)_2\text{NH}$ , but with no  $\text{CH}_3\text{NH}_2$  formation. 1,1-Dimethylhydrazine generates by pyrolysis  $\text{NH}_3$ ,  $\text{H}_2$ , and  $(\text{CH}_3)_2\text{NH}$ , while 1,2-dimethylhydrazine generates  $\text{NH}_3$ ,  $\text{H}_2$ ,  $\text{CH}_3\text{N}=\text{NCH}_3$ , and possibly some hydrocarbons, but no amines. Tetramethylhydrazine pyrolysis was studied in the range 447–657 °C with similar products formation [86]. The high pressure rate constants  $k^\infty$  for the four hydrazines follow Arrhenius equation with the parameters  $A$  and  $E^\ddagger$  shown in Table 14.5.1 [86].

TABLE 14.5.1. Parameters in Arrhenius equation for methylhydrazines [86]

Molecule	$A \text{ (s}^{-1}\text{)}$	$E^\ddagger \text{ (kcal)}$
Methylhydrazine $\text{CH}_3\text{NHNH}_2 \rightarrow \text{NH}_3$	$10^{13.2}$	54
Methylhydrazine $\text{CH}_3\text{NHNH}_2 \rightarrow \text{H}_2$	$10^{13.5}$	57
1,1-Dimethylhydrazine	$10^{17.0}$	63
1,2-Dimethylhydrazine	$10^{13.5}$	57
Tetramethylhydrazine	$10^{17.4}$	54

The decomposition mechanism of methylhydrazine and of 1,2-dimethylhydrazine seems to involve a concerted transfer of a hydrogen atom from  $\text{CH}_3$  to  $\text{NH}_2$  to form ammonia, while 1,1-dimethylhydrazine and tetramethylhydrazine seem to pyrolyze by a N–N bond scission. Pyrolysis of 1,1-dimethylhydrazine was evaluated in studies related to the formation of metal nitrides (e.g. GaN) used in electronic industry [87,88].

Phenylhydrazine decomposes by heating around  $300^\circ\text{C}$  for several hours following the reaction:



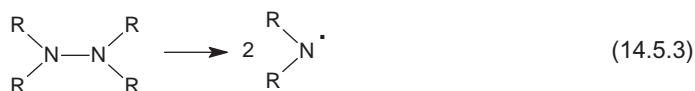
Thermal decomposition of a mixture of phenylhydrazine and phenylhydrazine hydrochloride at lower temperatures (around  $140^\circ\text{C}$ ) favors formation of aniline alone.

Thermal decomposition of 1,2-diphenylhydrazine (hydrazobenzene) around  $250^\circ\text{C}$  leads to the formation of azobenzene and aniline, as shown in the following reaction:



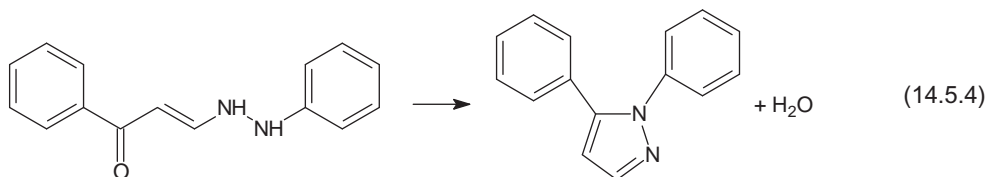
The same reaction as 14.5.2 is followed by other 1,2-aryl substituted hydrazines, such as *p,p'*-hydrazotoluene and several mixed 1,2-diarylhydrazines [89]. On the other hand, triphenylmethylhydrazine decomposes around  $220^\circ\text{C}$  to form  $\text{N}_2$  and triphenylmethane.

In the case of totally substituted hydrazines (similar to tetramethylhydrazine), the initial decomposition reaction takes place with the N–N bond dissociation as shown below:



The free radicals  $\text{R}_2\text{N}^\cdot$  generated in reaction 14.5.3 continue various reaction paths depending on the nature of the R substituents (which can be the same or different).

When other groups are present in the hydrazine molecule, they may or may not influence the outcome of pyrolysis. In these reactions, the formation of more stable compounds from the parent molecule is a determining factor, as also seen for many other compounds. For example, 1-phenyl-2-( $\beta$ -benzoylvinyl)hydrazine around  $185^\circ\text{C}$  at low pressure (14 Torr) generates 1,5-diphenylpyrazole:



2,4-Dinitrophenylhydrazine is another substituted hydrazine with additional functional groups. The compound is frequently used as a reagent for the analysis of carbonyl compounds [90]. Pyrolysis of a 0.5 mg sample of this compound was performed under flash conditions in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ . The pyrolysate was analyzed under conditions given in Table 4.6.1. The pyrogram is shown in Figure 14.5.1.

The peak identification is given in Table 14.5.2.

As shown in Table 14.5.2, the decomposition of 2,4-dinitro-phenylhydrazine is very similar to that of phenylhydrazine. The main pyrolysis product was 1,3-dinitrobenzene resulting from elimination of the  $\text{NH}-\text{NH}_2$  group. Other main pyrolysis results included nitroanilines, e.g. 3-nitroaniline and 2,4-dinitroaniline.

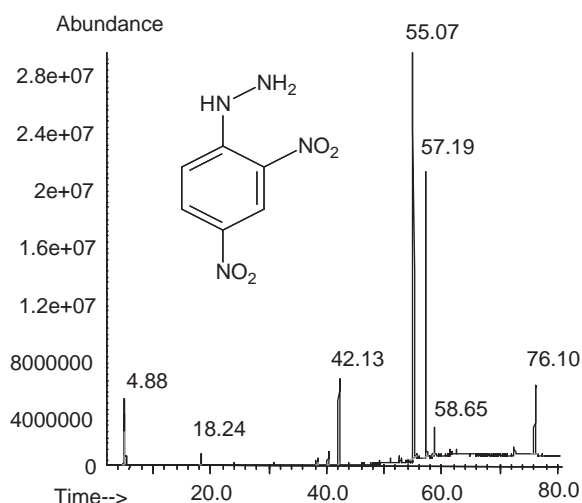


FIGURE 14.5.1. Pyrogram of 2,4-dinitrophenylhydrazine at 900 °C.

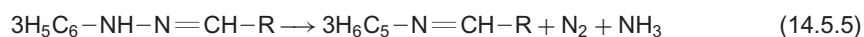
TABLE 14.5.2. Peak identification in the pyrogram shown in Figure 14.5.1 for pyrolysis of 2,4-dinitrophenylhydrazine

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Nitric oxide	4.88	30	10102-43-9	<b>9.92</b>
2	Carbon dioxide	4.97	44	124-38-9	<b>17.02</b>
3	Benzene	18.24	78	71-43-2	1.17
4	Aniline	38.16	93	62-52-3	0.30
5	Benzonitrile	38.51	103	100-47-0	0.43
6	Phenol	40.24	94	108-95-2	1.00
7	Nitrobenzene	42.13	123	98-95-3	<b>4.10</b>
8	5-Nitrobenzofurazan	50.97	165	18772-11-7	0.17
9	3-Nitrobenzonitrile	52.67	148	619-24-9	0.19
10	1,3-Benzenediol (resorcinol)	52.85	110	108-46-3	0.20
11	1,3-Dinitrobenzene	55.07	168	99-65-0	<b>44.47</b>
12	3-Nitroaniline	57.19	138	99-09-2	<b>14.22</b>
13	3-Nitrophenol	58.65	139	554-84-7	1.32
14	4-Nitroaniline	61.46	138	100-01-6	0.16
15	3-Nitro-1,1'-Biphenyl	62.37	199	2113-58-8	0.11
16	4-Nitro-1,2-Benzenediamine	72.52	153	99-56-9	0.18
17	2,4-Dinitroaniline	76.10	183	97-02-9	<b>5.05</b>

Notes: NH<sub>3</sub> was not analyzed due to the mass spectrometer settings.  
Mole percent of the main reaction products are in bold.

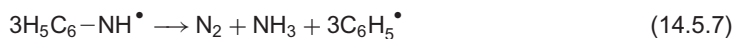
### Hydrazones

Hydrazones are compounds containing the group  $\text{>C=N-N<}$ , and they are typically generated by the elimination of a water molecule between a hydrazine and a carbonyl compound (aldehyde or ketone). Among the hydrazones derived from aldehydes, several phenylhydrazones were evaluated regarding their pyrolysis. The reactions taking place above 250 °C may follow several paths. A typical decomposition reaction is indicated below:

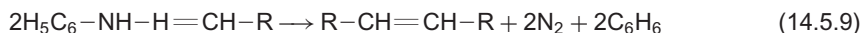




This reaction takes place by the cleavage of the N–N bond and formation of free radicals. As shown for oximes, the free radicals  $R-CH=N^\bullet$  were less reactive and slower to decompose compared to the free radicals  $H_5C_6-NH^\bullet$ , which easily decompose generating  $NH_3$  and other free radicals. The general path for reaction 14.5.5 is schematically shown below:



Other decomposition reactions of hydrazones also are encountered, usually generating minor constituents in the pyrolysate. One such reaction is the elimination of  $N_2$ , as shown below:



The structure of the R group, as well as of possible substituents on the aryl group (such as  $CH_3$ ,  $NO_2$ ,  $Cl$ ,  $COOH$ , etc.) may influence the outcome of pyrolysis. As an example, the results for the pyrolysis of 2,4-dinitro-phenylhydrazone of acetaldehyde are discussed below. The pyrolysis was performed on 0.2 mg sample under flash condition using Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900^\circ C$ ,  $\beta = 10^\circ C/ms$ , THT = 10 s, and housing temperature  $T_{hou} = 280^\circ C$ . The pyrolysate was analyzed under conditions given in Table 4.6.1. The pyrogram is shown in Figure 14.5.2.

The peak identification is given in Table 14.5.3. The formation of acetaldehyde in the pyrolysate shows that the pyrolysis of this compound does not follow the general trend indicated by reaction 14.5.4. The large level of  $CO_2$  shows that oxidation reactions due to the presence of  $NO_2$  substituents play an important role during pyrolysis.

1,2-Bis-hydrazones are obtained, for example, as a result of the reaction of a hydroxyaldehyde (or sugars) with phenylhydrazine. The first step in this reaction is the formation of a phenylhydrazone as a result of the reaction between the aldehyde group and the hydrazine, but the reaction continues with the oxidation of the sugar OH group to carbonyl and the reduction of one phenylhydrazine molecule into  $NH_3$  and aniline. The resulting bis-hydrazones are also known as osazones. Pyrolysis of dibenzoyl

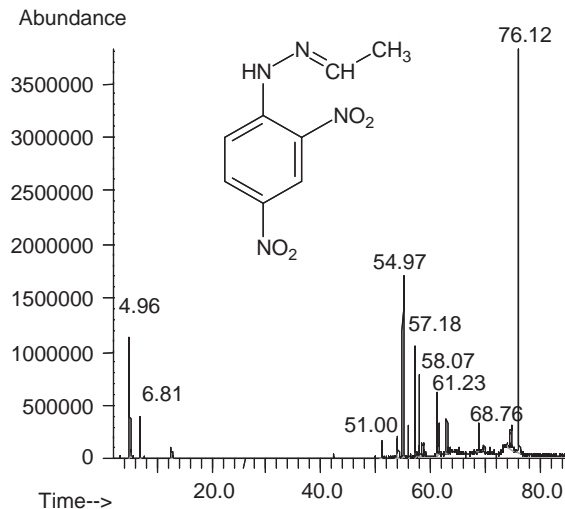


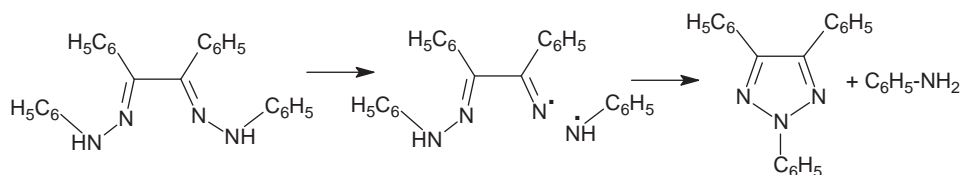
FIGURE 14.5.2. Pyrogram of 2,4-dinitrophenylhydrazone of acetaldehyde at  $900^\circ C$ .

TABLE 14.5.3. Peak identification in the pyrogram shown in Figure 14.5.2 for the pyrolysis of 2,4-dinitrophenylhydrazone of acetaldehyde

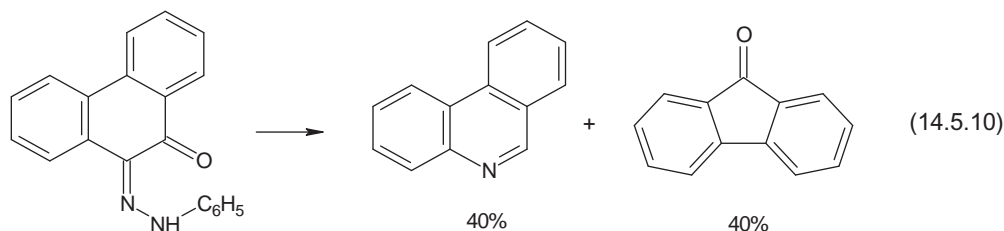
No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Nitric oxide	4.88	30	10102-43-9	<b>8.22</b>
2	Carbon dioxide	4.96	44	124-38-9	<b>31.15</b>
3	Acetaldehyde	6.81	44	75-07-0	<b>5.60</b>
4	5-Nitrobenzofurazan	51.00	165	18772-11-7	0.59
5	4-Nitro-1-isocyanatobenzene	53.85	164	100-28-7	0.59
6	2-Nitroaniline	54.11	138	88-74-4	0.70
7	1,3-Dinitrobenzene	54.97	168	99-65-0	<b>6.67</b>
8	2-Methyl-6-nitro[1.2.4]triazolo[1.5-a]pyridine	55.98	178	7169-92-8	0.99
9	3-Nitroaniline	57.18	138	99-09-2	<b>5.91</b>
10	3-(4-Nitrophenyl)-5H-1,2,4-triazole	58.07	190	N/A	2.84
11	2,3-Dimethyl-6-nitroquinoxaline?	61.23	203	2942-03-2	1.74
12	4-Nitroaniline	61.46	138	100-01-6	2.05
13	<i>N</i> -Ethyl- <i>N</i> -methyl-4-nitrobenzeneamine?	63.02	180	56269-48-8	1.25
14	1-Methyl-4-nitro-1H-indazole	68.76	177	26120-43-4	1.33
15	2,4-Dinitrophenylhydrazone of acetaldehyde	74.77	224	1019-57-4	3.46
16	2,4-Dinitroaniline	76.13	183	97-02-9	<b>26.91</b>

Notes: NH<sub>3</sub> was not analyzed due to the mass spectrometer settings.  
Mole percent of the main reaction products are in bold.

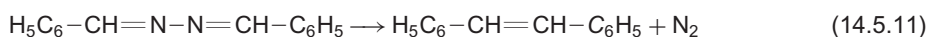
osazone (1,2-diphenylethanedione osazone) takes place as shown below:



Other hydrazones with more complex structures may generate different compounds, depending on the functional groups present in the molecule (see e.g. [53,55]). As an example, vacuum flash pyrolysis of 10-phenylhydrazone of phenanthren-9,10-dione generates by pyrolysis phenanthridine and fluoren-9-one:



The elimination of water between hydrazine and two molecules of a carbonyl compound leads to the formation of an aldazine with the general formula  $\text{>C=N-N=C<}$ . Thermal decomposition of benzaldazine generates N<sub>2</sub> and stilbene, as shown in the following reaction.



(It should be noted that benzaldazine is not obtained directly from benzaldehyde and hydrazine, but by the decarboxylation of its dicarboxy derivative synthesized from phenylglyoxilic acid and hydrazine).

### Other compounds related to hydrazines

Other hydrazine-related compounds were studied regarding their behavior during pyrolysis. Among these compounds are, for example, the nitramines, which have the general formula  $R_2N-NO_2$  where R can be H and/or an organic radical. These substances are of interest because some have been used as energetic materials (explosives). One such example is tetryl (2,4,6-trinitrophenyl-*N*-methylnitramine). Thermal decomposition of tetryl has been the subject of several studies [91,92]. A review on thermal behavior of nitramines showed that the first step in their decomposition is the cleavage of N- $NO_2$  bond [93]. Decomposition of furazan heterocycle with a nitramino substituent is also reported in the literature [94] (see Section 21.4). Pyrolysis of other compounds such as tetrazones, with the general formula  $R_2N-N=N-NR_2$  (these compounds can be included in different classes of nitrogenous compounds), also were reported [55].

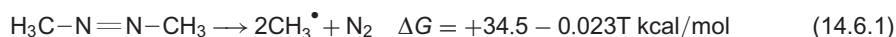
## 14.6. AZO, DIAZO, AND AZOXY DERIVATIVES

### General aspects

Azo derivatives (diazenes) are compounds with the general formula  $R-N=N-R'$ . The radicals R and R' can be alkyl or aryl and can be identical or different. Aliphatic azo derivatives are not very stable, and, for example, azomethane  $CH_3-N=N-CH_3$  decomposes by pyrolysis to generate free radicals  $CH_3^\bullet$ . Semiaromatic azo derivatives are more stable than the aliphatic ones, and azo-aromatic compounds are even more stable. Many organic dyes and pigments are azo-aromatic compounds because the azo group has strong chromophore properties. In the literature, the azo derivatives are sometimes indicated as diazo. However, the generally accepted formula for diazo compounds is  $R_2CN_2$ . For aromatic compounds, the diazonium salts with the formula  $R-N \equiv N^+ X^-$  (R aromatic) are common and widely used in the synthesis of many organic dyes.

### Azo derivatives

Azomethane  $CH_3-N=N-CH_3$  decomposes at temperatures around 450–500 °C to generate  $N_2$  and  $C_2H_6$ , and low levels of  $C_2H_4$  and  $CH_4$ . The initial reaction consists of the cleavage of the C–N bond and can be written as follows:



Arrhenius equation for reaction 14.6.1 evaluated in the temperature range 676–813 K has the following expression [95]:

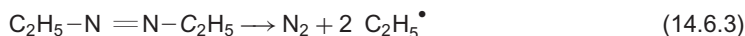
$$k \text{ (s}^{-1}\text{)} = 10^{13.3 \pm 0.3} \exp \left[ \frac{-189 \pm 4 \text{ (kJ/mol)}}{RT} \right] \quad (14.6.2)$$

Other studies on azomethane decomposition were done for the evaluation of reaction kinetics [96,97] as well as in relation to the generation of  $CH_3^\bullet$  free radicals for various purposes [98–105].

Besides the formation of  $CH_3^\bullet$  free radicals in azomethane decomposition, the formation of  $CH_2^\bullet-N=N-CH_3$  free radicals was considered [106], but these radicals play a small role in azomethane decomposition.

Azoethane thermal decomposition also is reported in the literature [107]. Decomposition of this compound generates  $C_4H_{10}$ ,  $C_2H_4$ , and  $C_2H_6$  and does not take place as cleanly as azomethane decomposition. Depending on the temperature and pressure, compounds such as ethyl 2-butyl diimide

and ethanal diethylhydrazone at levels below 2–3 mole % were detected in the pyrolysates performed at 293 °C and 29 Torr. The main reaction is still the formation of  $\text{C}_2\text{H}_5$  free radicals, which by termination reactions form hydrocarbons as shown below:



The reaction kinetics was found to follow the Arrhenius equation shown below [108]:

$$k \text{ (s}^{-1}\text{)} = 10^{15.7} \exp \left[ \frac{-(48.5 \text{ kcal})}{RT} \right] \quad (14.6.6)$$

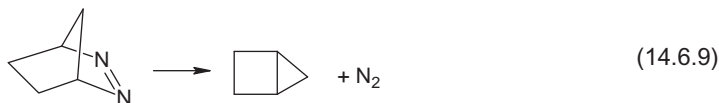
Among other azo alkyl derivatives studied regarding their pyrolysis are azoisobutane [109], hexafluoroazomethane [110,111], and perfluoroazo-2-propane [112]. Hexafluoroazomethane was studied in the temperature range 572–634 K in a static system at pressures between 0.3 Torr and 73 Torr, and the parameters for Arrhenius equation describing the decomposition was determined to have the form:

$$k \text{ (s}^{-1}\text{)} = 10^{10.17 \pm 0.15} \exp \left[ \frac{-(55.2 \pm 0.4 \text{ kcal})}{RT} \right] \quad (14.6.7)$$

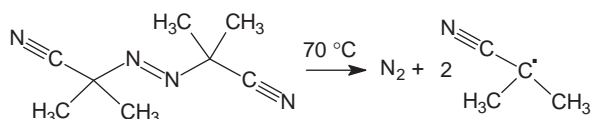
The Arrhenius equation for perfluoroazo-2-propane decomposition was found to be the following [112]:

$$\log_{10} k \text{ (s}^{-1}\text{)} = +16.7 \pm 0.2 - \frac{(9856 \pm 109)}{T} \quad (14.6.8)$$

The decomposition of azo compounds with the formation of free radicals and with little or no contribution from multiple initiation reactions has been used in organic synthesis. For example, synthesis of bicyclo[2.1.0]pentane can be achieved by thermal decomposition of 2,3-diazabicyclo[2.2.1]hept-2-ene at 180–195 °C in a reaction as shown below [113]:

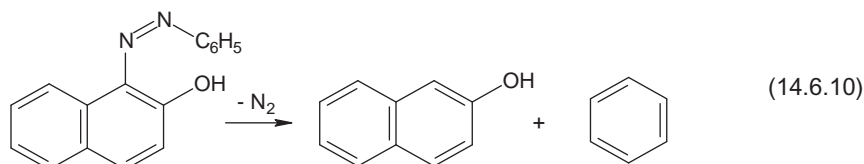


Azoisobutyronitrile, which decomposes around 70 °C, is used as a free radical initiator. The compound easily eliminates  $\text{N}_2$  and forms two 2-cyanoprop-2-yl free radicals. The reaction is shown below:

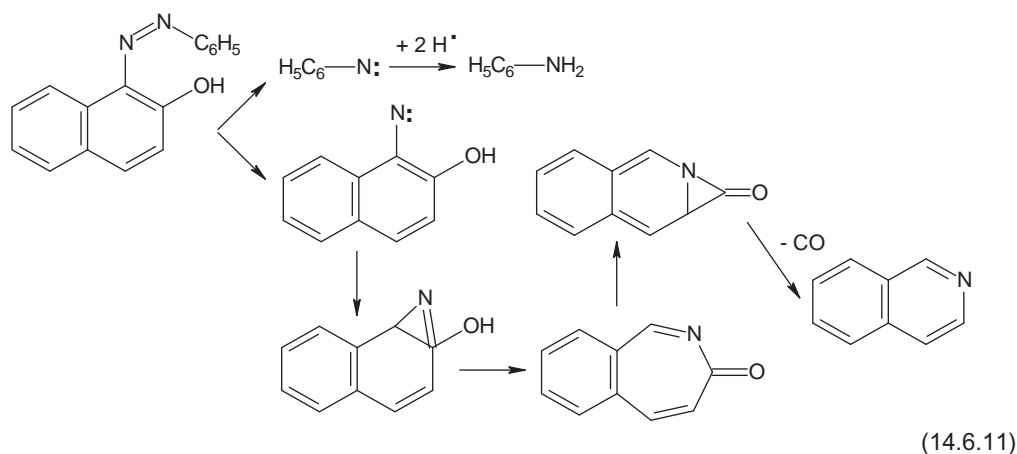


Aromatic azo compounds are thermally more stable than the aliphatic ones. Azobenzene, for example, is stable at temperatures as high as 400 °C. Above these temperatures decomposition starts with the formation of benzene, biphenyl, and some char.

When additional groups are present in the molecule, pyrolysis products of azo-aromatic compounds becomes more complicated since the free radicals formed from the initial reaction may suffer radical transfer reactions, hydrogen abstractions, etc. For example, pyrolysis of 4-(phenylazo)phenol and of several phenylazonaphthols using flash vacuum pyrolysis (FVP) at 700 °C and 0.02 Torr has been reported in the literature [53]. Pyrolysis of 4-(phenylazo)phenol generates the expected phenol and benzene, and pyrolysis of phenylazonaphthols generates the expected naphthols and benzene. These reactions involve the cleavage of the N–C bonds, and the pyrolysis of phenylazo-2-naphthol by this mechanism is shown below.

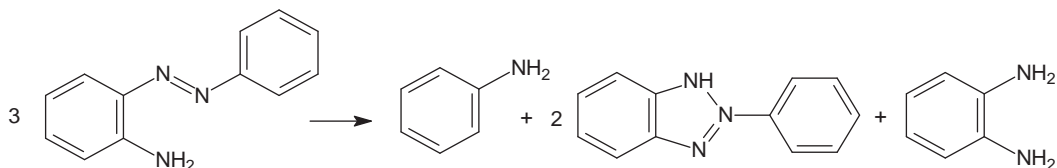


However, among the pyrolysis products for 4-(phenylazo)phenol are found pyridine and aniline, and for phenylazonaphthols are found aniline, quinoline, and isoquinoline. The formation of these compounds involve the cleavage of the N=N bond. The potential mechanism for the generation of the heterocycles involves the formation of azepines, as shown below:



For the formation of quinoline, the N: atom should bond to C9 and not to C2 of the naphthalene cycle as it does in reaction 14.6.11.

The presence of an NH<sub>2</sub> group in *o*-position to the azo group also leads to the formation of a variety of pyrolysis products including triazoles, as shown in the following reaction:



Many azo derivatives are used as dyes (azo dyes). Pyrolysis of a number of dyes and pigments has been used for their identification [114–116]. Some characteristic pyrolysis products of several types of azo dyes are given in Table 14.6.1 [115].

Some characteristic pyrolysis products of several individual dyes are given in Table 14.6.2 [114].

TABLE 14.6.1. Some characteristic pyrolysis products of several types of azo dyes [115]

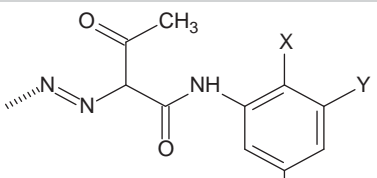
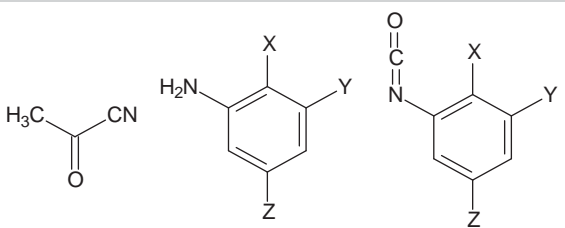
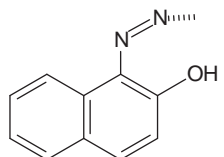
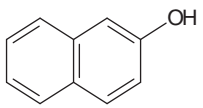
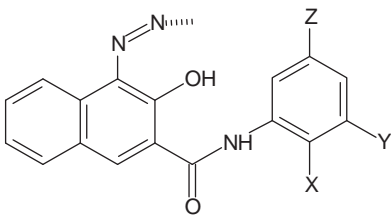
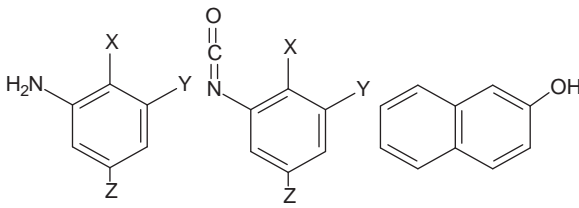
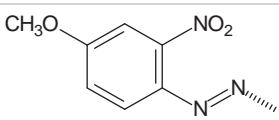
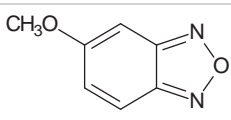
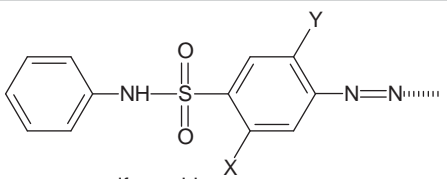
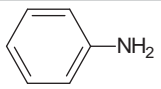
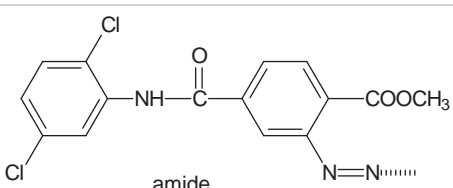
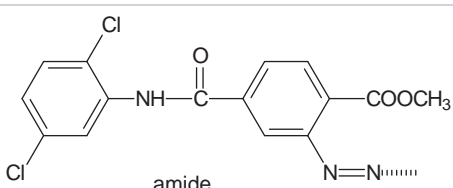
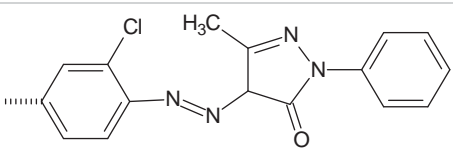
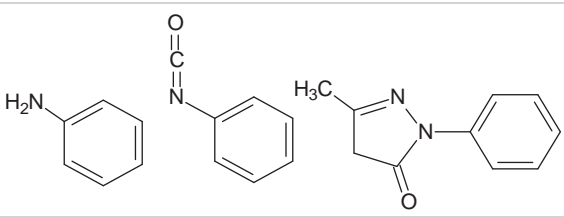
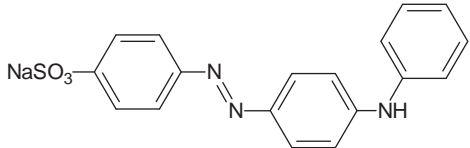
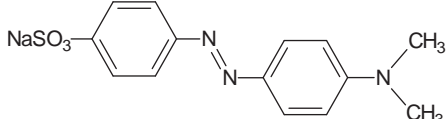
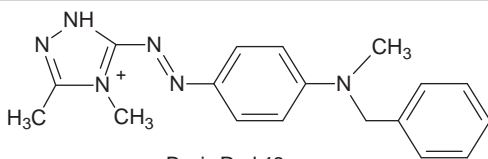
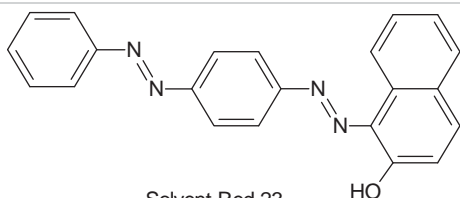
Dye type	Characteristic compound in pyrolysate
 acetoacetyl compounds	
 2-naphthol type compounds	
 2-hydroxy-3-naphthanilides	
 nitro compounds	
 sulfonamide	
 amide	 amide
 pyrazolone	

TABLE 14.6.2. Examples of specific azo dyes and their main pyrolysis products used for dye identification [114]

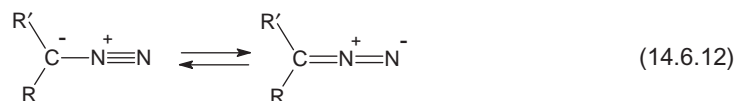
Dye	Temperature (°C)	Characteristic compound in pyrolysate
 <p>Acid Orange 5</p>	500–800	Aniline N-Phenylbenzene-1,4-diamine Diphenylamine SO <sub>2</sub> CO <sub>2</sub>
 <p>Acid Orange 52</p>	300–650	Aniline N,N-Dimethylbenzene-1,4-diamine 1,4-Benzenediamine SO <sub>2</sub> CO <sub>2</sub>
 <p>Basic Red 46</p>	500	4-Methyl-4H-1,2,4-triazol-3-yl-amine N-Benzyl-N-methylbenzene-1,4-diamine Benzylmethylphenylamine
 <p>Solvent Red 23</p>	500	4-Aminoazobenzene 1-Aminonaphthalene-2-ol Aniline

Besides the dyes shown in Tables 14.6.1 and 14.6.2, other dyes were also pyrolyzed and their typical fragment molecules identified and used for the dye identification. These include Reactive Orange 107-Original, Reactive Orange 16-Original, Reactive Orange 16-hydrolyzed, Reactive Black 5-Original, Reactive Black OH, Reactive Black NH<sub>2</sub>, Direct Blue 151, Direct Blue 71, Direct Brown 1, Solvent Red 26, etc. [114].

The azo group can be connected with other groups besides hydrocarbon radicals. For example, connection with NH group leads to diazoamino compounds with the formula R–N=N–NH–R. Phenyl-diazoamino-phenyl decomposes above 200 °C with formation of N<sub>2</sub> and aminobiphenyl [55].

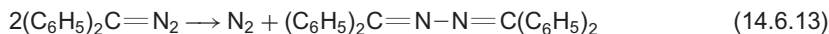
### Diazo derivatives and diazonium salts

Diazo derivatives are compounds with the general formula R<sub>2</sub>C=N<sub>2</sub>. The structure of these compounds can be expressed by the following equilibrium:



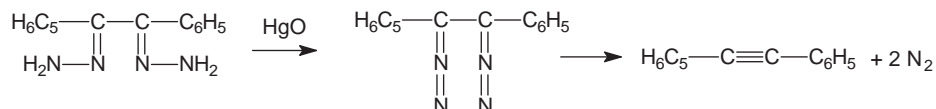
Diazomethane is a gas that decomposes slowly even at 0 °C and explodes when heated around 200 °C to generate N<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. Phenyl-diazomethane C<sub>6</sub>H<sub>5</sub>–CH=N<sub>2</sub> generates by mild heating

stilbene and  $N_2$ , and diphenyldiazomethane decomposes around  $115^\circ\text{C}$  with the formation of a cetazine as shown below:

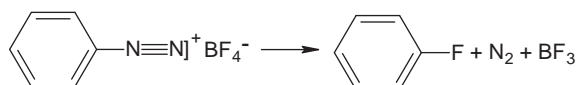


Somewhat more stable than other diazo derivatives is diazocyclopentadiene  $\text{C}_5\text{H}_4\text{N}_2$ , which decomposes at temperatures above  $200^\circ\text{C}$ .

Diazoderivatives can be the intermediate compounds in the oxidation of hydrazones (e.g. with  $\text{HgO}$ ), and thermal decomposition of bis-diazoderivatives can be used to generate alkynes as shown in the following reaction:

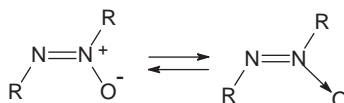


The action of acids on aliphatic diazo compounds typically leads to their rapid decomposition. However, the aromatic diazo compounds form somewhat more stable diazonium salts with the general formula  $\text{R}-\text{N}\equiv\text{N}]^+ \text{X}^-$ . These compounds decompose easily at temperatures around  $100^\circ\text{C}$  generating  $\text{N}_2$  and  $\text{RX}$ . In the case of fluoroborate  $\text{BF}_4^-$  as an anion, the reaction takes place with the formation of fluorinated compounds as shown in the following reaction:

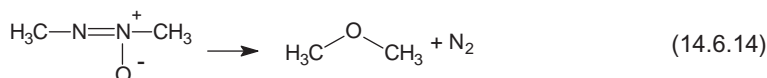


### Azoxy compounds

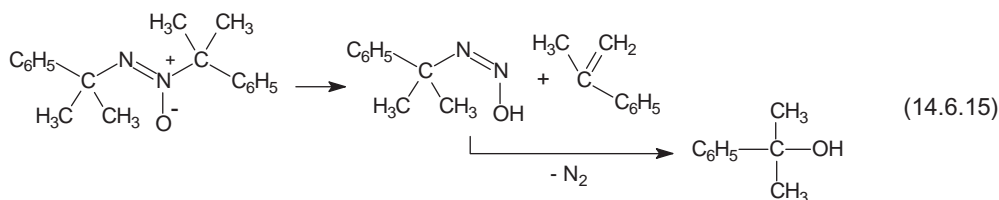
Azoxy compounds contain in their molecule a bond similar to amine N-oxides, and their formula can be described by the following two structures (a coordinate covalent bond is indicated as " $\rightarrow$ "):



The two R radicals in azoxy compounds (same or different) can be hydrocarbon type (aromatic or aliphatic) but also alkoxy (e.g. methoxy), tosyl (*p*-toluenesulfonyl), etc. Azoxy compounds are relatively stable, compared to their azo equivalents. For example, azoxyisobutyronitrile is stable up to about  $180^\circ\text{C}$ , while the corresponding azo derivative decomposes at  $80^\circ\text{C}$ . Pyrolysis of azoxy compounds usually leads to the elimination of  $\text{N}_2$ , as shown for the pyrolysis of azoxymethane (at  $600^\circ\text{C}$ ) in a reaction as shown below [117]:

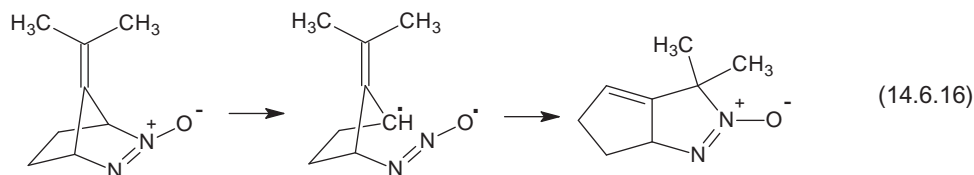


In other pyrolysis reactions of azoxy compounds, an alcohol is generated, as shown below for azoxyisopropylbenzene, which decomposes around  $190^\circ\text{C}$ :

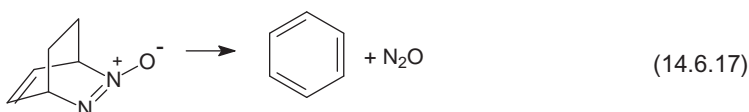




Reaction 4.6.15 indicates that upon heating, similar to the case of some azo derivatives, the N–C bond is cleaved in azoxy compounds and not the N→O bond [118]. Various studies showed that the N–C bond that breaks is the one close to the oxygen. This is exemplified in the following rearrangement that takes place by heating of 7-(methylethylidene)-2,3-diazabicyclo[2.2.1]hept-2-ene [119]:



During pyrolysis of azoxy compounds, loss of N<sub>2</sub>O is not typical (that would be similar to the loss of N<sub>2</sub> from azo derivatives) [118]. However, in some instances the formation of N<sub>2</sub>O takes place as shown in the following reaction:



Formation of N<sub>2</sub> ( $\Delta H^\circ = 0$  kcal/mol) is typically favored to the formation of N<sub>2</sub>O ( $\Delta H^\circ = +19.7$  kcal/mol).

Studies on the pyrolysis of azoxy compounds connected to methoxy groups [120] or tosyl [121] also were reported in the literature.

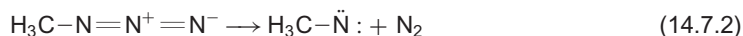
## 14.7. AZIDES

### General aspects

The organic azides (diazo-imino derivatives) are compounds with the general formula R–N<sub>3</sub>, and some compounds from this group are potentially explosive compounds (some azides are used as drugs, such as azidothymidine). Many azides are relatively stable to heating. Methyl azide (CH<sub>3</sub>N<sub>3</sub>) decomposes only about 1% at temperatures around 200 °C and with explosion at 500 °C. The reaction products include N<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, H<sub>2</sub>, and low levels of other compounds such as HCN [122]. The decomposition rate is described by the following Arrhenius equation (for the high pressure constant):

$$k^\infty (\text{s}^{-1}) = 2.85 \cdot 10^{14} \exp \left[ \frac{-40.5 (\text{kcal})}{RT} \right] \quad (14.7.1)$$

The initial step in the reaction is the formation of N<sub>2</sub> and of a methyl nitrene CH<sub>3</sub>–N̈ that cannot be isolated. The reaction is shown below:

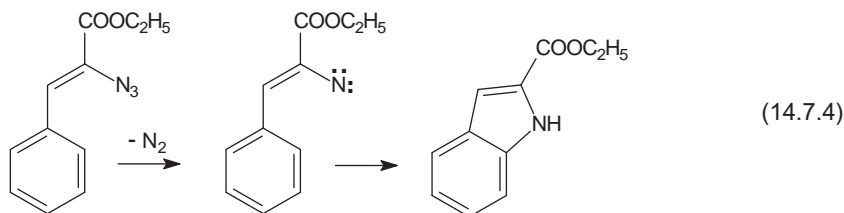


The nitrene further undergoes various reactions that are responsible for other pyrolysis components. One possible reaction is the conversion of the nitrene into a methanimine, which further decomposes, for example with the formation of HCN and H<sub>2</sub> as shown below [123]:

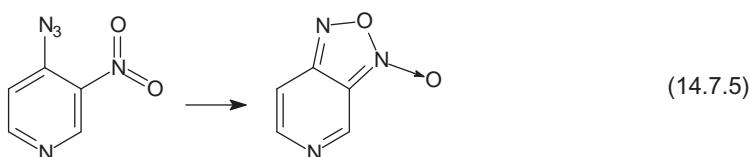


Several other studies were performed for the understanding of methyl azide thermal decomposition [124,125].

Azides with a more complex structure, which by pyrolysis eliminate  $N_2$  and generate nitrene, continue the transformation process, and generate new compounds, typically containing cycles as shown in the following reaction [126]:

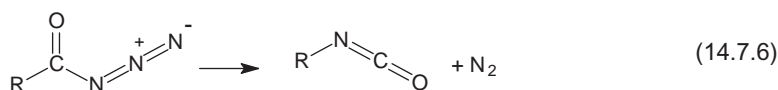


Similar reactions were noticed for other azides. Formation of a furazan-1-oxide was, for example, obtained from 4-aza-3-nitropyridine as shown below [127]:



Similar reactions were noticed for other azanitropyridines and quinolines [127]. Various similar reactions were reported in the literature [55].

The azide group can be connected not only to a hydrocarbon radical, but also to an acyl group. The compounds from this class eliminate  $N_2$  upon heating, but also suffer a rearrangement (known as Curtius rearrangement [128]) with the formation of isocyanates. This reaction is shown below [129, 130]:



The mechanism of this reaction involves the elimination of  $N_2$  and formation of an acyl nitrene, which suffers the rearrangement by the migration of the R group to the nitrogen atom.

Kinetic parameters regarding azides thermal decomposition were reported for a number of other azides [131–136].

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## CHAPTER 15

*Pyrolysis of Aldehydes and Ketones***15.1. ALDEHYDES****General aspects**

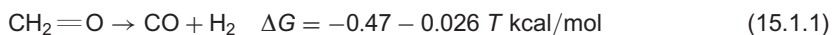
Aldehydes are carbonyl compounds with the general formula  $R-CH=O$ , where  $R$  is a hydrocarbon radical. The carbonyl functional group  $>C=O$  is bonded in aldehydes to a hydrogen atom and to a carbon atom. Several naming procedures are used for aldehydes. A standard procedure starts with the name of the longest carbon chain containing the aldehyde group and replacing the suffix *-e* with *-al* (e.g., methanal, ethanal, etc.). It is also common to name the aldehyde starting with the name of the acid from which the aldehyde derives (by the replacement of the  $COOH$  group with the  $CHO$  group). This is done by changing the suffix *-ic acid* or *-oic acid* with *-aldehyde* (e.g., formaldehyde from formic acid, acetaldehyde from acetic acid, etc.) In other procedures, the  $CHO$  group is indicated by the suffix *carboxaldehyde* or by the prefix *oxo-*.

The aldehydes are very common compounds, being found in nature and being synthesized for numerous applications. The aldehyde group can be present in more complex molecules, including carbohydrates (where the  $CHO$  group is free or is present in acetal form). Due to the importance and complexity of carbohydrates, their pyrolysis is discussed separately in Chapter 16.

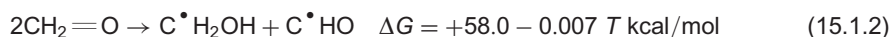
The aldehydes are the result of many oxidation processes, including the oxidation of carburants that takes place in flames. Pyrolysis of aldehydes has been the subject of numerous studies.

**Formaldehyde**

Formaldehyde starts to decompose at temperatures above  $450^\circ C$ . Pyrolysis performed in the temperature range  $466\text{--}516^\circ C$  showed that the decomposition reaction has approximately a second order rate [1]. The main pyrolysis products are  $CO$  and  $H_2$ , and the reaction can be written as follows:



In addition to  $CO$  and  $H_2$ , lower levels of methanol were also detected in the pyrolysate. The level of methanol is higher at lower temperatures of pyrolysis. Among the compounds that were not formed by pyrolysis at lower temperatures were  $CO_2$ , formic acid, glyoxal, dimethyl ether, and methane. At lower temperatures, the initiation reaction appears to be the following:



The rate constants for the formation of  $CO$ ,  $H_2$ , and  $CH_3OH$  in the temperature range  $466\text{--}516^\circ C$  were found to be described by the following Arrhenius equations [1] ( $R$  in cal):

$$k_{CO} = 10^{11.8 \pm 0.4} \exp \left[ \frac{-(34400 \pm 1300)}{RT} \right] \text{ cc}^{0.8} / (\text{mol}^{0.8} \text{ s}) \quad (15.1.3)$$

$$k_{H_2} = 10^{8.7 \pm 1.0} \exp \left[ \frac{-(34000 \pm 3600)}{RT} \right] \text{ cc}^{0.6} / (\text{mol}^{0.6} \text{ s}) \quad (15.1.4)$$

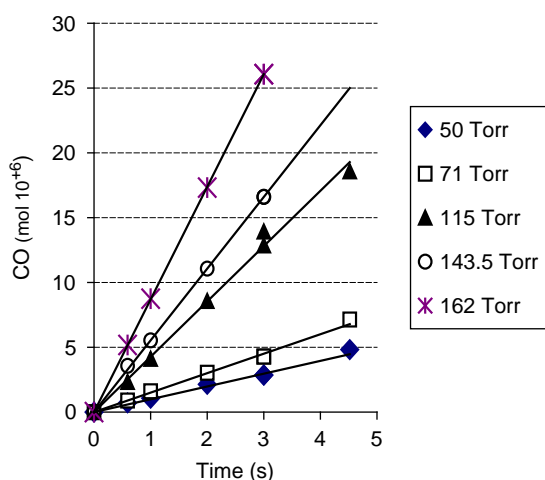


FIGURE 15.1.1. The variation of CO yield at 516.6 °C and different CH<sub>2</sub>O pressures as a function of decomposition time [1].

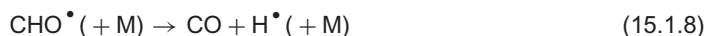
$$k_{\text{CH}_3\text{OH}} = 10^{12.6 \pm 0.9} \exp \left[ \frac{-(36800 \pm 3600)}{RT} \right] \text{ cc}/(\text{mol s}) \quad (15.1.5)$$

The variation of CO yield at 516.6 °C and different CH<sub>2</sub>O pressures as a function of decomposition time is shown in Figure 15.1.1.

As temperature increases, methanol is formed only in traces, and in the range between 930 °C and 1730 °C, the initiation takes place by the following reaction:



This reaction is followed by propagation reactions as follows:



and by the termination reactions:



The parameters for the Arrhenius equation in the form  $k = A T^n \exp(-E^a/RT)$  (units: cm, mol, cal, K) for the reactions 15.1.6–15.1.10 are given in Table 15.1.1 [2,3].

Some other studies were performed regarding pyrolysis of formaldehyde. These include shock waves experiments [4–6], modeling studies [7], laser heating pyrolysis [8], etc.

Oxidation of formaldehyde has been studied in various conditions [9,10]. The oxidation starts with initiation reaction of the type:

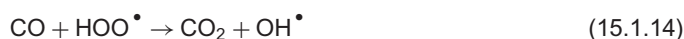
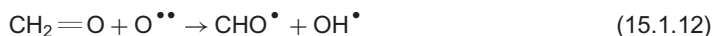


The free radicals formed in these reactions or directly from oxygen that can generate under the influence of heat free O<sup>••</sup> atoms continue with propagation reactions that generate CO, CO<sub>2</sub>, water, and

TABLE 15.1.1. The parameters for the Arrhenius equation in the form  $k = A T^n \exp(-E^a/RT)$  (units: cm, mol, cal, °K) for the reactions 15.1.6–15.1.10 [2,3]

Reaction	A	n	E <sup>a</sup>
15.1.6	$5.54 \times 10^{15}$	0	75000
15.1.7	$2.18 \times 10^8$	1.77	3000
15.1.8	$6.95 \times 10^{17}$	-1	17000
15.1.9	$2.16 \times 10^{14}$	0	0
15.1.10	$4.50 \times 10^{13}$	0	0

other free radicals as shown in the following examples:



Specific values for the kinetic parameters for these reactions are reported in the literature [2]. When sufficient oxygen is present, the overall result of the process can be written as follows:

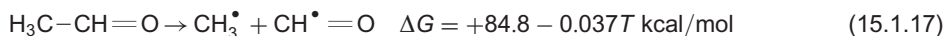


At lower temperatures, reaction 15.1.16 can take place without the formation of CO as an intermediary species [10].

### Acetaldehyde

Pyrolysis of acetaldehyde at temperatures higher than 725 °C generates mainly CO and CH<sub>4</sub> with lower levels of H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>2</sub>H<sub>4</sub>. The results obtained performing pyrolysis in a turbulent flow reactor at 778 °C using CH<sub>3</sub>CHO at a level of about 1% in nitrogen at different exposure times are shown in Figure 15.1.2 [11].

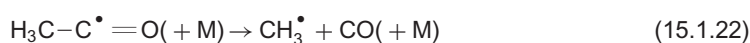
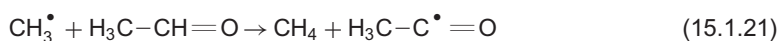
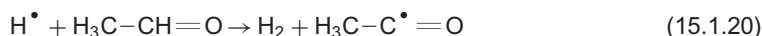
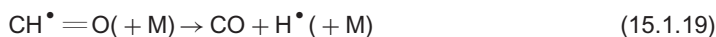
Traces of acetone, propane, propene, and acetylene were also detected in the pyrolysate above 725 °C. The pyrolysis process starts with the following initiation reaction:



At temperatures in the range 525–725 °C, the Arrhenius equation for reaction 15.1.17 was found to be [11]:

$$k \text{ (s}^{-1}\text{)} = 10^{15.85 \pm 0.2} \exp \left[ \frac{(-81775 \pm 1000)}{RT} \right] \quad (15.1.18)$$

The process continues with various propagation reactions as shown below:





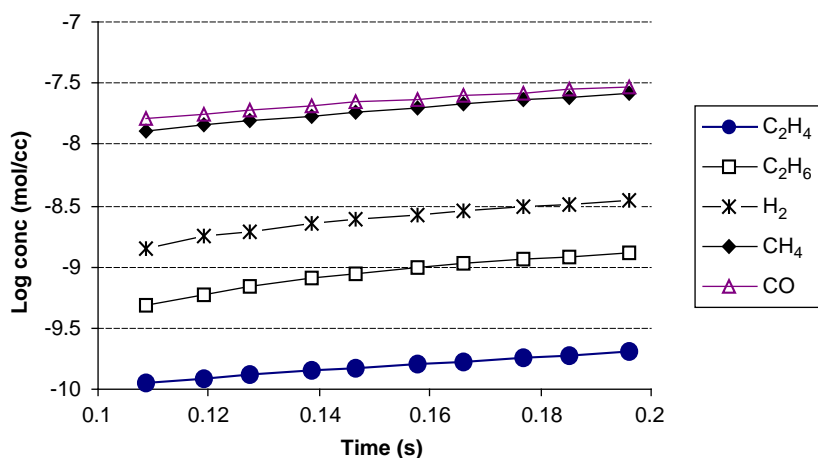


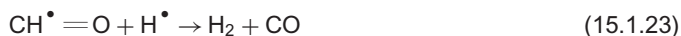
FIGURE 15.1.2. Results for pyrolysis of acetaldehyde in a turbulent flow reactor at 778°C using  $\text{CH}_3\text{CHO}$  at a level of about 1% in nitrogen at different exposure times [11].

TABLE 15.1.2. The parameters for the Arrhenius equation  $k = A T^n \exp(-E^a/RT)$  for the reactions 15.1.17–15.1.25 [12]

Reaction*	Log A	$n$	$E^a$ kcal/mol
15.1.17 $k^\infty$	22.632	-1.88	85.48
15.1.17 $k^0$	76.346	-11.81	95.04
15.1.19	13.602	0	15.535
15.1.20	13.375	0	3.642
15.1.21	-3.150	4.58	1.966
15.1.22	15.780	0	14.070
15.1.23	?	0	0
15.1.24	13.301	0	0
15.1.25	13.023	0	0

\*For reaction 15.1.17, an  $F_{\text{cent}} = 0.601 T^{-0.162} \exp(-1.07/RT)$  calculated from Troe parameters was obtained [12].

Also, termination reactions lead to the formation of CO,  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_6$  as shown below:



At higher temperatures, acetaldehyde pyrolysis has been evaluated using shock tube experiments with partial pressures in the range 40–500 Torr and temperatures in the range 1275–2125 °C [12–14]. The diluting gas used in the experiment was krypton. The reaction 15.1.17 being unimolecular, a limiting high pressure rate constant  $k^\infty$  as well as low pressure rate constant  $k^0$  were determined (see also Section 3.2). The values for these constants are given in Table 15.1.2. The parameters for the Arrhenius equation in the form  $k = A T^n \exp(-E^a/RT)$  for the reactions 15.1.19–15.1.25 are also given in Table 15.1.2 [12].

Other studies were also performed on acetaldehyde pyrolysis and are reported in the literatures [15–17].

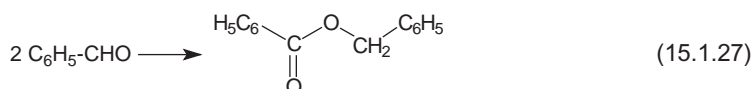
**Benzaldehyde**

Benzaldehyde decomposes at temperatures above 500 °C with the formation of CO and benzene in a reaction as shown below:

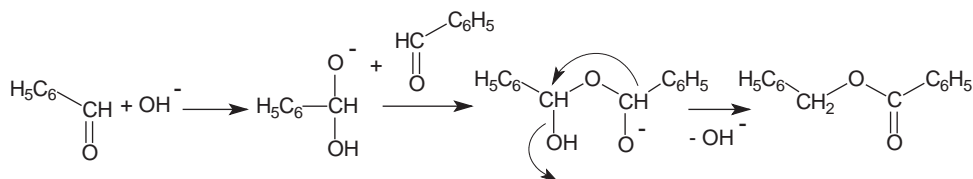


At higher temperatures, besides CO and benzene, small amounts of H<sub>2</sub>, biphenyl, and char are generated.

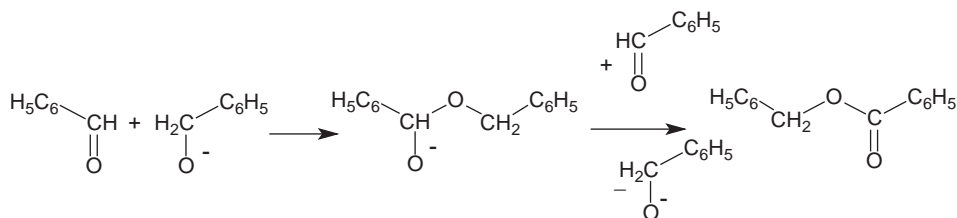
At lower temperatures, in the range 350–370 °C, pyrolysis in a glass-sealed tube of benzaldehyde leads to the formation of benzyl benzoate in a reaction similar to a Cannizzaro disproportionation:



Cannizzaro reaction typically takes place in a basic medium with the formation of an anion as shown below:



In the pyrolysis process, with no OH<sup>−</sup> added (by purpose), it is possible that either impurities or the glass walls of the pyrolysis vessel serves as a source of OH<sup>−</sup> anions. Also, since an autocatalytic effect on this reaction was proven for benzyl alcohol, the formation of small amounts of benzyl alcohol may be the reason for the formation of benzyl benzoate. In this case, the reaction takes place as shown below:



where the benzyolate ion is formed from the dissociation of benzyl alcohol.

**Other simple aldehydes**

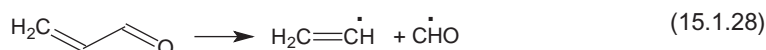
Propionaldehyde decomposes upon heating above 500 °C, mainly with the formation of CO and ethane (in a similar reaction with that of acetaldehyde). Relative to the composition of acetaldehyde pyrolysate, the levels of hydrogen and methane are higher because of a higher extent of side reactions. At temperatures between 450 °C and 600 °C, the reaction has a unimolecular mechanism, and at higher temperatures, the pyrolysis process becomes more complex, with an increase in the yield of methane.

Pyrolysis of some other aldehydes that generate stable hydrocarbons decompose similarly to acetaldehyde with a few side reactions. This is the case, for example, for 2,2,2-triphenylethanal, which generates CO and triphenylmethane, and that of cinnamic aldehyde, which generates mainly CO and styrene (with lower levels of benzene, acetylene, ethylene, and distyrene [18]).

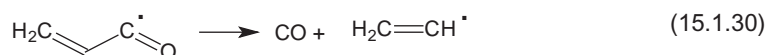
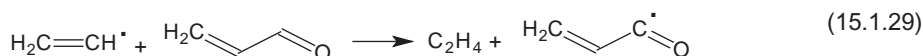
On the other hand, pyrolysis of 2-methylpropanal (isobutyraldehyde) around 600 °C, besides producing CO, does not form as expected mainly propane. A mixture of gases is generated, including H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> as the main components, and also some propene, and ethylene [18]. Similarly, pyrolysis of 3-methylbutanal (isovaleraldehyde) forms CO, CH<sub>4</sub>, H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and a mixture of other saturated and unsaturated hydrocarbons. The formation of free radicals by reactions similar to reaction 15.1.17 and further interactions of these free radicals explain the result of the process.

Pyrolysis of acrolein (2-propenal), at 530 °C in a static system, also generates a mixture of products including CO, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>4</sub>H<sub>8</sub>, and other hydrocarbons. For example, pyrolysis of acrolein diluted in the mole ratio 2:1 with toluene or benzene generated by pyrolysis, the results shown in Table 15.1.3, expressed in mole percent product/mole acrolein reacted [19].

In addition to the compounds listed in Table 15.1.3, acetylene, propyne, propane, 2-butenes, isoprene, cyclohexane, and dihydropyran were detected in the pyrolysate. The initiation of acrolein decomposition is similar to that of acetaldehyde and is described by the following reaction:



The reaction is followed by propagation reactions of the type:



The free radicals formed in these reactions are the source of the compounds listed in Table 15.1.3 and of other trace compounds found in acrolein pyrolysate.

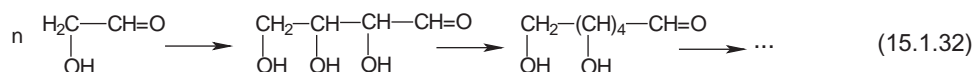
In the presence of oxygen, pyrolysis of acrolein generates similar compounds as pyrolysis in a nonoxidizing atmosphere, plus some acetaldehyde and water. The formation of C<sub>2</sub>H<sub>3</sub><sup>•</sup> free radicals during acrolein pyrolysis and their reaction with O<sub>2</sub> may be the source of acetaldehyde. Other free radicals such as OH<sup>•</sup> and OOH<sup>•</sup> may also play a role in this process.

TABLE 15.1.3. Composition of acrolein pyrolysate expressed in mole percent product/mole acrolein reacted [19]

Compound	Acrolein in toluene (heating time 4 s, temp. 600 °C)	Acrolein in benzene (heating time 9.8 s, temp. 600 °C)
CO	86–97	100
C <sub>2</sub> H <sub>4</sub>	22–24	20
C <sub>3</sub> H <sub>6</sub>	8.7–9.2	12
H <sub>2</sub>	7.2–8.3	2
CH <sub>4</sub>	5.4–6.2	2
C <sub>2</sub> H <sub>6</sub>	3.3–4.4	3
1,3-Butadiene	3.4	2
1-Butene	2.3–3.0	3
C <sub>3</sub> H <sub>8</sub>	–	2

### Hydroxyaldehydes

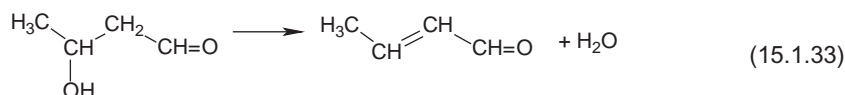
Hydroxyaldehydes are common compounds, the class of carbohydrates being included in this type of compounds. Pyrolysis of carbohydrates is discussed separately in Chapter 16. Even excluding carbohydrates, numerous other compounds have both the OH and the CHO functionalities. These functionalities can be positioned on the same carbon (e.g., glycolaldehyde), or they can be in  $\beta$ ,  $\gamma$ , etc. position. Glycolaldehyde (or hydroxyacetaldehyde) is not stable to heating, and keeping around 100 °C for several hours undergoes a condensation of the type:



At higher temperatures, glycolaldehyde decomposes with the formation of various small molecules including CO and CH<sub>3</sub>OH. Lactaldehyde by low temperature heating forms some acetol, and at higher temperatures generates various decomposition products including CO, ethanol, acrolein, etc.

Pyrolysis of glycolaldehyde in the presence of tetramethylammonium hydroxide (TMAH) shows that the substance undergoes an aldol condensation in strong basic medium provided by TMAH. The resulting condensation products include C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub> carbohydrates. Further reactions during thermally assisted hydrolysis and methylation generate compounds similar to those obtained from glucose, which include several methylated metasaccharinic (deoxyaldonic) acids [20] (see Chapter 16).

$\beta$ -Hydroxyaldehydes easily eliminate water by mild heating (around 165 °C), a typical reaction being the transformation of aldols in homologs of crotonaldehyde, as shown below for aldol (3-hydroxybutyraldehyde):



The reaction is also associated with decomposition and formation of acetaldehyde by a retro-aldol condensation (see Section 2.3). Heating at higher temperatures leads to decomposition with the formation of small molecules including CO, CH<sub>4</sub>, small chain alkanes and alkenes, etc. Other aldols undergo reactions similar to reaction 15.1.33 upon mild heating, and at higher temperatures suffer decompositions with formation of H<sub>2</sub>O, CO, and small chain hydrocarbons.

### Aldehydes containing hydroxy and ether groups

Compounds with various functional groups such as alcohol, ether, and aldehyde are common in nature. For example, 4-hydroxy-3-methoxybenzaldehyde (vanillin) contains aldehyde, alcohol, and ether groups. This compound is present in nature and also synthesized as a flavorant. Pyrolysis of a sample of vanillin was performed on 0.50 mg compound using Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900$  °C,  $\beta = 10$  °C/ms, THT = 10 s, and housing temperature  $T_{\text{hou}} = 280$  °C. The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The window between 36.0 min and 60.0 min from the pyrogram is given in Figure 15.1.3, and the compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 15.1.4. The calculation of the mole percent was obtained based solely on peak areas, and since differences in the MS response factors can be quite large for different compounds, the estimations may have large errors.

The peak of vanillin dominates the pyrogram, because a large amount of compound vaporizes before reaching the decomposition temperature. Vanillin peak area was not included in the calculation of molar contribution to pyrolysate. From Table 15.1.4, it can be seen that formation of 2-methoxyphenol with elimination of CO from the aldehyde group in vanillin, similar to reaction 15.1.26, is an important

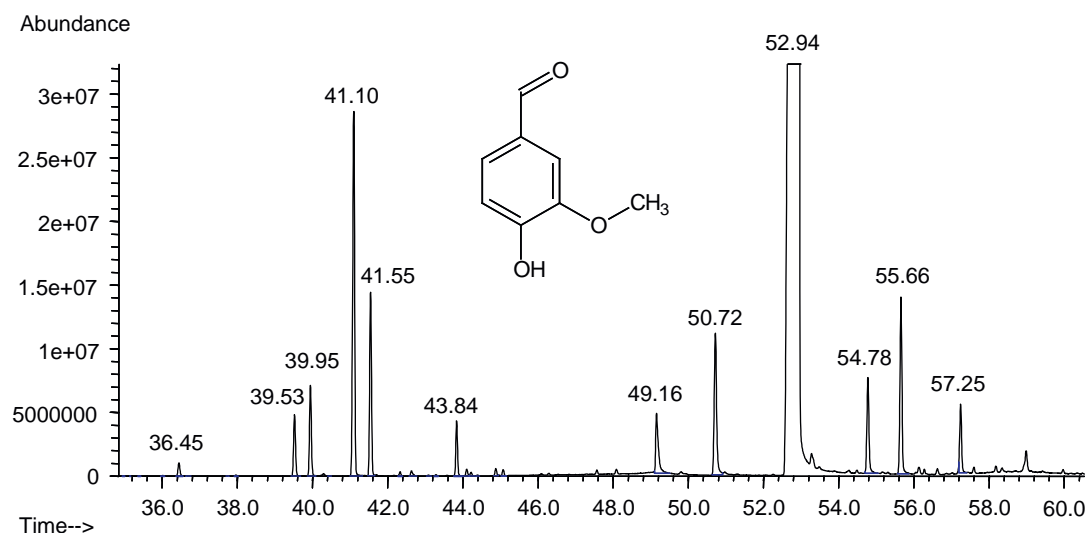
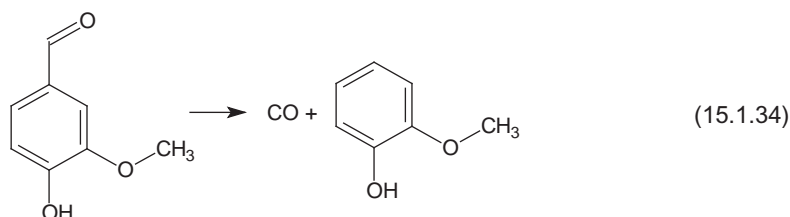
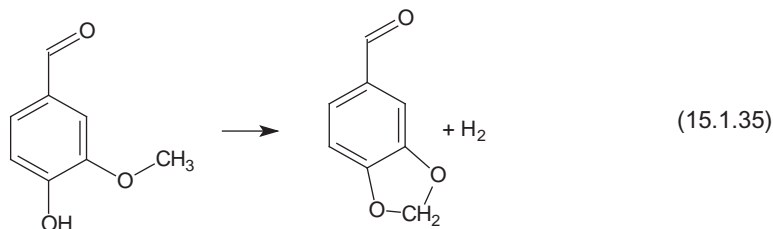


FIGURE 15.1.3. Window 36–60 min of the pyrogram for 4-hydroxy-3-methoxybenzaldehyde (vanillin).

component of the pyrolysis process. This reaction is shown below:



The level of 2-methoxyphenol that can be found in the pyrolysate is 27.4%, and it is possible that more 2-methoxyphenol was initially generated but that it was further decomposed in the pyrolytic process. The ether group does not decompose before the aldehyde to generate a phenol and a hydrocarbon (see reaction 10.4.2). The corresponding compound that would be generated for vanillin is 3,4-dihydroxybenzaldehyde, which was not detected in the pyrolysate. On the other hand, 1,2-benzenediol (catechol) was detected in the pyrolysate, the likely reactions that generate this compound being the decomposition of 2-methoxyphenol in a similar decomposition to that of methoxybenzene (see reaction 10.4.1). Another reaction taking place during vanillin pyrolysis is that leading to the formation of piperonal, shown as follows:



The elimination of hydrogen and the formation of 9.66% piperonal in the pyrolysate indicate that the phenol group also decomposes in a reaction similar to that of phenol (see reaction 9.3.1) and the phenoxy radical further generates piperonal. The formation of 4-hydroxy-3-methyl-benzaldehyde and other compounds with a methyl group attached to the benzene ring is additional proof that complex radicalic reactions take place during vanillin pyrolysis. Pyrolysis of vanillin deposited on  $\text{Al}_2\text{O}_3$

TABLE 15.1.4. Identification of the main peaks in the chromatogram shown in Figure 15.1.3 for the pyrolysis of 4-hydroxy-3-methoxybenzaldehyde (vanillin) (hydrogen, CO, methane, ethane, and water not included)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Carbon dioxide	4.71	44	124-38-9	2.73
2	1,3-Butadiene	5.86	54	106-99-0	0.50
3	1,3-Cyclopentadiene	9.55	66	542-92-7	0.23
4	Benzene	17.88	78	71-43-2	0.20
5	Toluene	24.41	92	108-88-3	0.31
6	Styrene	31.26	104	100-42-5	0.20
7	2-Cyclopenten-1-one	31.75	82	930-30-3	0.22
8	Benzofuran	36.45	118	271-89-6	0.88
9	2-Hydroxybenzaldehyde	39.53	122	90-02-8	3.96
10	Phenol	39.95	94	108-95-2	7.49
11	2-Methoxyphenol	41.10	124	90-05-1	24.70
12	2-Methylphenol	41.55	108	95-48-7	12.92
13	2,3-Dimethylphenol	42.34	122	526-75-0	0.23
14	4-Methylphenol	42.64	108	106-44-5	0.42
15	2-Ethylphenol	43.84	122	90-00-6	3.22
16	3,4-Dimethylphenol	44.11	122	95-65-8	0.42
17	2-Methoxy-5-methylphenol	44.22	138	1195-09-1	0.20
18	2,3-Dihydrobenzofuran	44.88	120	496-16-2	0.45
19	3-Methoxybenzaldehyde	45.08	136	591-31-1	0.33
20	3-Methyl- <i>para</i> -anisaldehyde	47.57	150	32723-67-4	0.20
21	2,3-Dihydro-1H-inden-1-one	48.09	132	83-33-0	0.27
22	1,2-Benzenediol (catechol)	49.16	110	120-80-9	6.84
23	3,4-(Methylenedioxy)benzaldehyde (piperonal)	50.72	150	120-57-0	9.66
24	2-Methylbenzofuran	50.98	132	4265-25-2	0.22
25	4-Hydroxy-3-methoxybenzaldehyde (vanillin)	52.94	152	121-33-5	Not included
26	3,4-Dimethoxybenzaldehyde	53.28	166	120-14-9	1.10
27	4-Hydroxybenzaldehyde	54.78	122	123-08-0	6.93
28	4-Hydroxy-3-methylbenzaldehyde	55.66	136	15174-69-3	10.94
29	9H-xanthene	56.63	182	92-83-1	0.25
30	4-Methyl- <i>para</i> -anisaldehyde	57.25	150	32723-67-4	3.95

has the effect of decomposing a much larger proportion of the parent molecule, with the formation of H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>3</sub>-O-CH<sub>3</sub>, CH<sub>3</sub>-OH, and 3,4-dimethoxybenzaldehyde as the main decomposition products.

Another aldehyde containing alcohol and ether groups, which is similar to vanillin, is syringaldehyde or 4-hydroxy-3,5-dimethoxybenzaldehyde. This compound is found in some types of wood (spruce, maple, etc.). Pyrolysis of a sample of syringaldehyde was performed on 0.75 mg compound using Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900^{\circ}\text{C}$ ,  $\beta = 10^{\circ}\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280^{\circ}\text{C}$ . The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The window between 38.0 min and 62.0 min from the pyrogram is given in Figure 15.1.4, and the compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 15.1.5. The calculation of the mole percent was obtained based solely on peak areas.

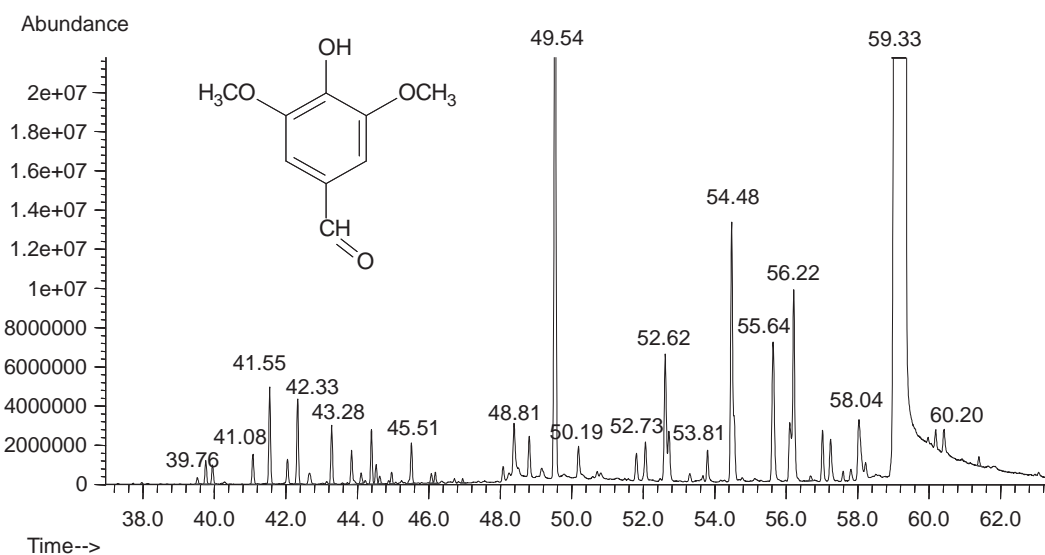


FIGURE 15.1.4. Window 38–62 min of the pyrogram for 4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde).

TABLE 15.1.5. Identification of the main peaks in the chromatogram shown in Figure 15.1.4 for the pyrolysis of 4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde) (hydrogen, CO, methane, ethane, and water not included)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Carbon dioxide	4.70	44	124-38-9	7.00
2	Propene	4.97	42	115-07-1	0.37
3	Formaldehyde	5.20	30	50-00-0	0.77
4	Propyne	5.31	40	74-99-7	0.39
5	2-Butene	5.61	56	107-01-7	0.12
6	1,3-Butadiene	5.85	54	106-99-0	0.18
7	1,2-Butadiene	6.26	54	590-19-2	0.18
8	Methanol	7.05	32	67-56-1	2.59
9	Cyclopentene	8.12	68	142-29-0	0.06
10	1,4-Pentadiene	8.83	68	591-93-5	0.09
11	1,3-Cyclopentadiene	9.53	66	542-92-7	0.28
12	1,4-Cyclohexadiene	14.90	80	628-41-1	0.13
13	1-Methyl-1,3-cyclopentadiene	15.47	80	96-39-9	0.10
14	3-Methylenecyclopentene	17.20	80	930-26-7	0.07
15	Benzene	17.88	78	71-43-2	0.23
16	Toluene	24.41	92	108-88-3	0.39
17	Ethylbenzene	29.15	106	100-41-4	0.02
18	1,3-Dimethylbenzene ( <i>m</i> -xylene)	29.55	106	108-38-3	0.10
19	1,4-Dimethylbenzene ( <i>p</i> -xylene)	30.86	106	106-42-3	0.02
20	Styrene	31.25	104	100-42-5	0.03
21	2-Methyl-2-cyclopenten-1-one	33.98	96	1120-73-6	0.27

TABLE 15.1.5. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
22	Benzofuran	36.45	118	271-89-6	0.27
23	3-Hydroxybenzaldehyde	39.52	122	100-83-4	0.23
24	2-Methylbenzofuran	39.76	132	4265-25-2	0.80
25	Phenol	39.95	94	108-95-2	0.93
26	7-Methylbenzofuran	40.21	132	17057-52-8	0.03
27	2-Methoxyphenol	41.08	124	90-05-1	1.09
28	2-Methylphenol	41.55	108	95-48-7	4.12
29	2-Hydroxy-4-methylbenzaldehyde	42.05	136	698-27-1	0.78
30	2,6-Dimethylphenol	42.33	122	576-26-1	3.26
31	3-Hydroxybenzeneethanol	42.66	138	13398-94-2	0.51
32	2,7-Dimethylbenzofuran	43.15	146	28715-26-6	0.07
33	3-Methyl-4-methoxyphenol	43.28	138	14786-82-4	1.90
34	2-Ethylphenol	43.83	122	90-00-6	1.35
35	2,4-Dimethylphenol	44.10	122	105-67-9	0.41
36	2-Ethyl-5-methylphenol	44.39	136	1687-61-2	1.67
37	1-(2-Hydroxy-5-methylphenyl)ethanone	44.52	150	1450-72-2	0.51
38	1,4-Dimethoxy-2-methylbenzene	44.62	152	24599-58-4	0.18
39	2,3-Dihydrobenzofuran	44.88	120	496-16-2	0.07
40	2,3,6-Trimethylphenol	44.96	136	2416-94-6	0.30
41	3-Hydroxy-4-methylbenzaldehyde	45.08	136	57295-30-4	0.03
42	4-Ethyl-2-methoxyphenol	45.51	152	2785-89-9	1.18
43	7-Methoxybenzofuran	46.07	148	7168-85-6	0.25
44	2-Ethyl-4,5-dimethylphenol	46.18	150	2219-78-5	0.27
45	1,2,3-Trimethoxybenzene	46.94	168	634-36-6	0.09
46	2,2,-Bifuran	48.08	134	5905-00-0	0.51
47	3-Methoxy-1,2-benzenediol	48.40	140	934-00-9	0.89
48	2-Hydroxy-3-methoxybenzaldehyde	48.78	152	148-53-8	0.82
49	2,6-Dimethoxyphenol	49.54	154	91-10-1	25.24
50	2-Methylbenzofuran-3-carboxaldehyde	51.81	160	55581-61-8	0.87
51	4-Hydroxy-3-methoxybenzaldehyde (vanillin)	52.62	152	121-33-5	4.74
52	6-Hydroxy-4-methoxy-2,3-dimethylbenzaldehyde	53.80	180	34883-12-0	0.76
53	4,6-Dihydroxy-2,3-dimethylbenzaldehyde	54.48	166	2990-31-0	9.87
54	1-( <i>p</i> -Methoxyphenyl)-2-methoxyprop-1-ene	54.56	178	64304-85-4	0.92
55	4-Hydroxy-3-methylbenzaldehyde	55.64	136	15174-69-3	4.50
56	3-Methyl-methoxybenzaldehyde	55.68	150	32723-67-4	2.21
57	3,4,5-Trimethoxybenzaldehyde	56.11	196	86-81-7	1.74
58	3-Methoxy-4,5-methylenedioxybenzaldehyde	56.22	180	5780-07-4	6.46
59	2,3-Dimethyl- <i>para</i> -anisaldehyde	57.02	164	38998-17-3	1.51
60	4-Vinyl-2-methoxyphenol	57.25	150	7786-61-0	1.55
61	3-Methoxycinnamic acid	57.82	178	4/3/6099	0.29
62	4-Methyl-2,5-dimethoxybenzaldehyde	58.04	180	N/A	2.70
63	4-Hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde)	59.33	182	134-96-3	Not included
64	1-(4-Hydroxyphenyl)-3-phenyl-2-propen-1-one?	59.83	224	2657-25-2	0.48
65	4-Hydroxy-3,5-dimethoxybenzoic acid	60.20	212	884-35-5	0.24



Similar to the case of vanillin, the peak of syringaldehyde dominates the pyrogram because a large amount of compound vaporizes before reaching the decomposition temperature. Syringaldehyde peak area was not included in the calculation of molar contribution of pyrolysate. A variety of decomposition products are seen in Table 15.1.5, very similar to those found in vanillin pyrolysate. These include compounds resulting from the elimination of CO from the aldehyde group (2,6-dimethoxyphenol), compounds resulting from the cleavage of the ether group, as well as numerous compounds resulting from various rearrangement reactions. The phenolic OH group is more resistant to heating, as seen from the large number of phenolic compounds listed in Table 15.1.5. However, even these groups can be eliminated by heating, and simple molecules such as benzene and toluene are detected in the pyrolysate. It was not possible to determine if in these molecules the initial benzene ring was preexistent (to pyrolysis) or was synthesized from other smaller fragments.

## 15.2. KETONES

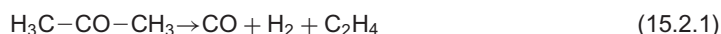
### General aspects

Ketones are carbonyl compounds with the general formula  $R-(CO)-R'$ , where R and R' are hydrocarbon radicals. The carbonyl functional group  $>C=O$  is bonded in ketones to two carbon atoms. Several naming procedures are used for ketones. A common name is derived from the name of the two radical groups R and R' and the word ketone. The IUPAC name recognizes the  $=O$  group (not  $C=O$ ) and changes the suffix "e" of the corresponding hydrocarbon (longest carbon chain) with the suffix "one," possibly indicating the position of the  $=O$  group with the lowest number (e.g., methyl ethyl ketone is butan-2-one). In some compounds with more important structural descriptors than ketone, the group  $=O$  can be indicated as "oxo" or "keto." Some traditional names are also used (e.g., acetone).

Ketones are important chemical compounds. They are present in nature and are synthesized for many applications. Ketones are used mainly as solvents and intermediates in chemical industry. Pyrolysis of ketones may occur in incinerators, in unintentional fires, as well as in some synthetic procedures such as the preparation of ketene [21]. (The name ketene is used for  $CH_2=CO$ , which is the simplest member of the class of compounds named ketenes.)

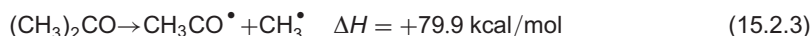
### Acetone

Pyrolysis of acetone,  $CH_3-CO-CH_3$ , has been performed in various conditions, which are reported in the literature [18,22–27]. The pyrolysis process generates CO,  $H_2$ ,  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_2H_2$ , and various other short chain hydrocarbons as well as ketene. In the interval 1100–1570 K, besides  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_2H_2$ , and ketene, the short chain hydrocarbons included propyne, allene, propene, and 1,3-butadiene. The main reactions in acetone decomposition can be written as follows:



In a shock tube experiment performed on 1% acetone vapors in argon, the variation in the ratios of concentration C to the initial acetone concentration  $C_0$  for several pyrolysis components is given in Figure 15.2.1 (the effective heating time was not the same for different temperatures, varying linearly between 2287  $\mu s$  at 1090 K and 1724  $\mu s$  at 1566 K) [28].

The decomposition of acetone occurs starting with the radical initiation reactions as shown below:



The kinetics of this reaction is described by the Arrhenius equation with parameters given in Table 15.2.1. The initiation is followed by several propagation steps:



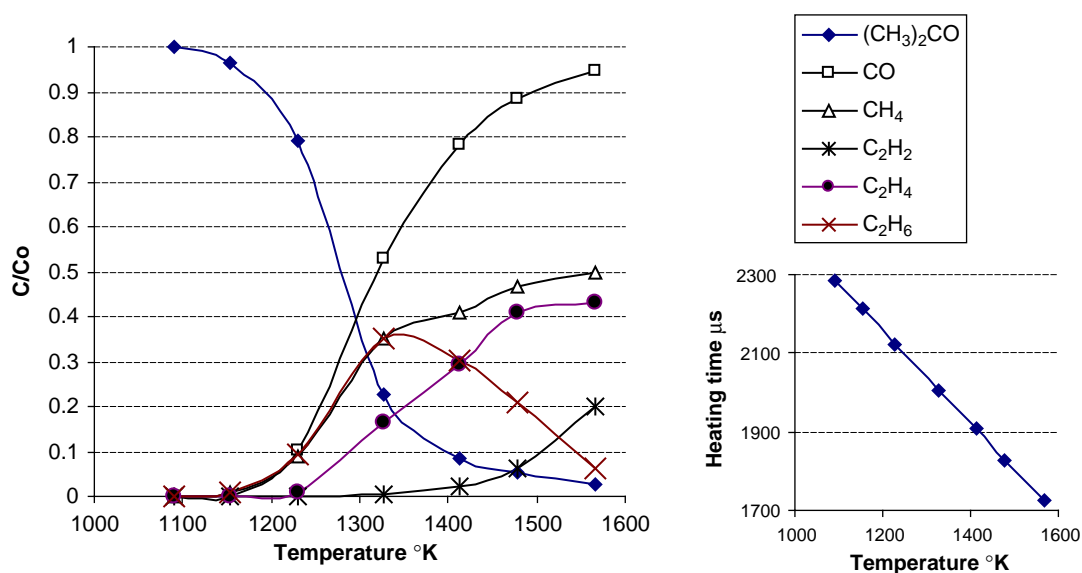
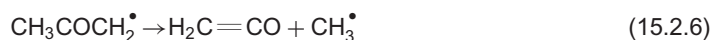


FIGURE 15.2.1. Variation with temperature in the ratios of concentration  $C$  to the initial acetone concentration  $C_0$  of several components of acetone pyrolysate. The linear dependence of effective heating time with the temperature is also shown.

TABLE 15.2.1.  $A$ ,  $n$  and  $E^a$  parameters in Arrhenius equation  $k = A T^n \exp(-E^a/RT)$  for reactions 15.2.3–15.2.6 and for several other reactions important in acetone pyrolysis

Reaction	$A^*$	$n$	$E^a$ kcal/mol
$\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_3\text{CO}^\bullet + \text{CH}_3^\bullet$	$1.13 \times 10^{16}$	0	81.7
$\text{CH}_3\text{COCH}_3 + \text{H}^\bullet \rightarrow \text{CH}_3\text{COCH}_2^\bullet + \text{H}_2$	$2.3 \times 10^7$	2	5.0
$\text{CH}_3\text{CO}^\bullet + (\text{M}) \rightarrow \text{CH}_3^\bullet + \text{CO} + (\text{M})$	$5.36 \times 10^{27}$	3.4	18.9
$\text{CH}_3\text{COCH}_3 + \text{CH}_3^\bullet \rightarrow \text{CH}_3\text{COCH}_2^\bullet + \text{CH}_4$	$9.50 \times 10^3$	2.5	8.4
$\text{CH}_3\text{COCH}_2^\bullet \rightarrow \text{CH}_2\text{CO} + \text{CH}_3^\bullet$	$1.0 \times 10^{13}$	0	28.0
$\text{CH}_3^\bullet + \text{CH}_3^\bullet \rightarrow \text{C}_2\text{H}_6$ $k_0^*$	$2.12 \times 10^{50}$	-9.7	5.2
$\text{CH}_3^\bullet + \text{CH}_3^\bullet \rightarrow \text{C}_2\text{H}_6$ $k^\infty^*$	$2.12 \times 10^{16}$	-1.0	0.62
$\text{C}_2\text{H}_6 + \text{H}^\bullet \rightarrow \text{C}_2\text{H}_5^\bullet + \text{H}_2$	$1.15 \times 10^8$	1.9	7.53
$\text{C}_2\text{H}_5^\bullet + \text{H}^\bullet \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$	$4.50 \times 10^{13}$	0	0.0

\*Troe parameters 0.5325, 151, 1038, 4970 (see Section 3.2).



The corresponding  $A$ ,  $n$ , and  $E^a$  parameters in Arrhenius equation  $k = A T^n \exp(-E^a/RT)$  for reactions 15.2.3–15.2.6 and for several other reactions important in acetone pyrolysis are given in Table 15.2.1. A number of termination reactions, also shown in Table 15.2.1, lead to the formation of  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ , and other short chain hydrocarbons.

In addition to the main initiation reaction 15.1.3, the decomposition of acetone may also start with the following initiation:

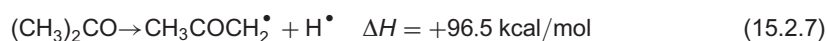


TABLE 15.2.2. Several main reactions taking place during acetone oxidation and the corresponding  $A$ ,  $n$ , and  $E^a$  parameters in Arrhenius equation  $k = A T^n \exp(-E^a/RT)$

Reaction	$A$	$n$	$E^a$ kcal/mol
$\text{CH}_3\text{COCH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{COCH}_2^\bullet + \text{HOO}^\bullet$	$6.0 \times 10^{13}$	0	51.9
$\text{CH}_3\text{COCH}_3 + \text{O}^{\bullet\bullet} \rightarrow \text{CH}_3\text{COCH}_2^\bullet + \text{OH}^\bullet$	$1.0 \times 10^{13}$	0	5.96
$\text{CH}_3\text{COCH}_3 + \text{OH}^\bullet \rightarrow \text{CH}_3\text{COCH}_2^\bullet + \text{H}_2\text{O}$	$2.0 \times 10^{13}$	0	3.0

However, this reaction has a much lower role in acetone pyrolysis, the dissociation enthalpy for the C–H bond being considerably higher than that in reaction 15.2.3.

The formation of ketene and  $\text{CH}_4$  in acetone pyrolysis is similar to the formation of CO and  $\text{CH}_4$  in the pyrolysis of acetaldehyde. Ketene can further decompose under the influence of heat, and it is difficult to determine the true extent of reaction 15.2.6 ( $\Delta H = +31.6$  kcal/mol) that leads to the amount of ketene detected in the pyrolysate. The formation of ketene during acetone pyrolysis can be used for the preparation of this compound [29].

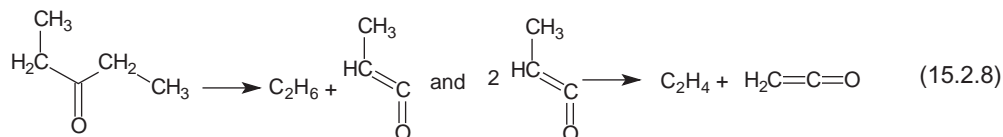
The study of acetone pyrolysis at very high temperature (4000 K) using shock wave experiments shows that the compound is completely decomposed within 3  $\mu\text{s}$  with the formation of  $\text{C}_2$  [25].

Acetone oxidation below 800 °C was also reported in the literature [28,30–32]. Table 15.2.2 shows three main reactions taking place during acetone oxidation and the corresponding  $A$ ,  $n$ , and  $E^a$  parameters in Arrhenius equation  $k = A T^n \exp(-E^a/RT)$ .

Once the oxidation process starts and a large number of free radicals are generated, numerous other propagation and termination reactions will take place. Acetone oxidation was simulated using computer modeling that involved 164 elementary reactions, including oxidation for formaldehyde, methane, ethane, ethylene, acetylene, and ketene [28]. Acetone has an enthalpy of combustion of 402 kcal/mol (at 25 °C) when the reaction generates  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

### Other ketones

Pyrolysis of methyl ethyl ketone and diethyl ketone takes place similarly to that of acetone. The compounds generated include CO,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_2$ , and other short chain unsaturated hydrocarbons. The formation of ketenes is also noticed during pyrolysis of these ketones around 700 °C, but the yield of methyl ketene ( $\text{CH}_3\text{--CH=C=O}$ ) is low, and ketene is formed in place by a reaction as shown below:



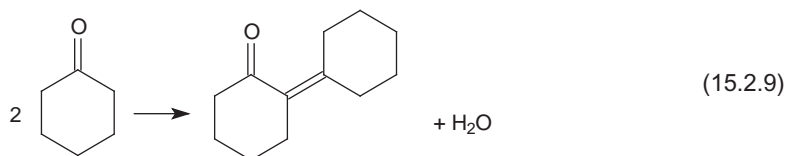
Decomposition of *tert*-butyl methyl ketone occurs only at temperatures above 700 °C. The reaction products are CO,  $\text{H}_2$ , and some other small hydrocarbons. The formation of ketene was also noticed but at very low level. Methane is not a main reaction product in the pyrolysis of *tert*-butyl methyl ketone.

Acetophenone ( $\text{C}_6\text{H}_5\text{--CO--CH}_3$ ) decomposes with the formation of CO (70–75%),  $\text{CO}_2$ , benzene, and lower levels of toluene, diphenyl, 1,4-diphenylbenzene,  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_4$ . The absence of a hydrogen atom on the aromatic carbon bound to the carbonyl group leads to the low levels of  $\text{CH}_4$  that are formed from more than one reaction involving free radicals. Triphenylbenzene, 1,3-diphenyl-2-buten-1-one, and traces of 2,4-diphenylfuran were generated when acetophenone was heated for a long time at low temperature (200 °C) [18].

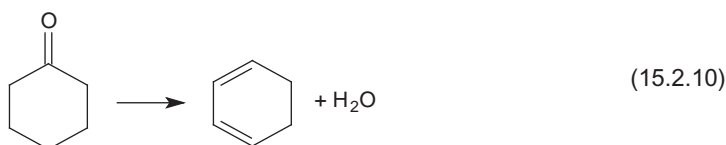
Thermal decomposition of dibenzyl ketone, or 1,3-diphenylacetone ( $\text{C}_6\text{H}_5\text{--CH}_2)_2\text{CO}$ , at temperatures above 400 °C leads to the formation of CO, toluene, and char. Small levels of short chain aliphatic hydrocarbons are also generated [18].

Cyclohexanone at temperatures above 700 °C decomposes with the formation of CO and various alkenes including  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ , etc. Smaller levels of other hydrocarbons such as  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{C}_2\text{H}_6$ , etc. are

also formed. Depending on the heating temperature, other reactions may also take place during cyclohexanone thermal decomposition. At lower temperatures (around 200 °C and long heating time), the formation of 2-cyclohexylidenecyclohexan-1-one was noticed [18]:



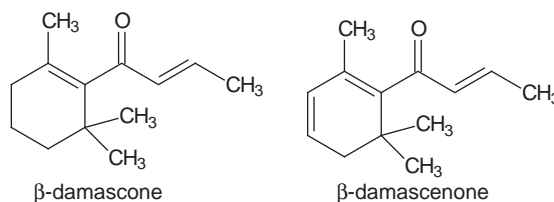
At higher temperature, the elimination of water takes place from a single cyclohexanone molecule with the formation of cyclohexadiene as shown below:



Benzophenone (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CO is the simplest aromatic ketone. This compound, at temperatures above 500 °C, generates mainly CO, benzene, diphenylmethane, and char. Pyrolysis of dibenzosuberone generates anthracene, CO, and H<sub>2</sub> as shown in reaction 2.3.7 [33].

When the molecule of the ketone becomes more complicated, the overall structure starts to play a more important role in the production of various components in the pyrolysate.

Two examples of ketones that are found in rose oil are  $\beta$ -damascone and  $\beta$ -damascenone.  $\beta$ -Damascone is (*E*)-1-(2,6,6-trimethyl-1-cyclohexenyl)but-2-en-1-one, and  $\beta$ -damascenone is (*E*)-1-(2,6,6-trimethyl-1-cyclohexa-1,3-dienyl)but-2-en-1-one. In the pyrolysis products of the two compounds at 900 °C using conditions similar to Type 1 Experiment as described in Section 4.6, the parent compound is present at more than 75% from the initial material. This is caused, in part, by the relatively good thermal stability of both  $\beta$ -damascone and  $\beta$ -damascenone, but mainly by their volatility such that during pyrolysis, a large amount of the parent compound volatilizes before reaching the equilibrium temperature  $T_{eq}$ . Among the pyrolysis products of both these ketones are present low levels of simple aromatic hydrocarbons such as toluene, 1,3-dimethylbenzene, 1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene, and some isomers of the parent molecule. Although the two ketones differ by only one additional double bond in the six-carbon cycle, the pyrolysis products show some qualitative and quantitative differences.



### Diketones and quinones

Two (or more) ketone groups can be present in the same molecule, and when present on an aliphatic chain, the ketone groups can be in positions 1,2 ( $\alpha$ ), 1,3 ( $\beta$ ), or separated by more carbon atoms. The simplest  $\alpha$ -diketone is diacetyl or butandione, CH<sub>3</sub>(CO)(CO)CH<sub>3</sub>. The decomposition of this compound at temperatures between 600 °C and 675 °C leads to the formation of CO, CH<sub>4</sub>, and ketene. The maximum yield of ketene is obtained around 615 °C [34].

The simplest  $\beta$ -diketone is acetylacetone or pentane-2,4-dione, CH<sub>3</sub>(CO)CH<sub>2</sub>(CO)CH<sub>3</sub>. The decomposition of this compound also leads to the formation of ketene and CH<sub>4</sub>. The optimum

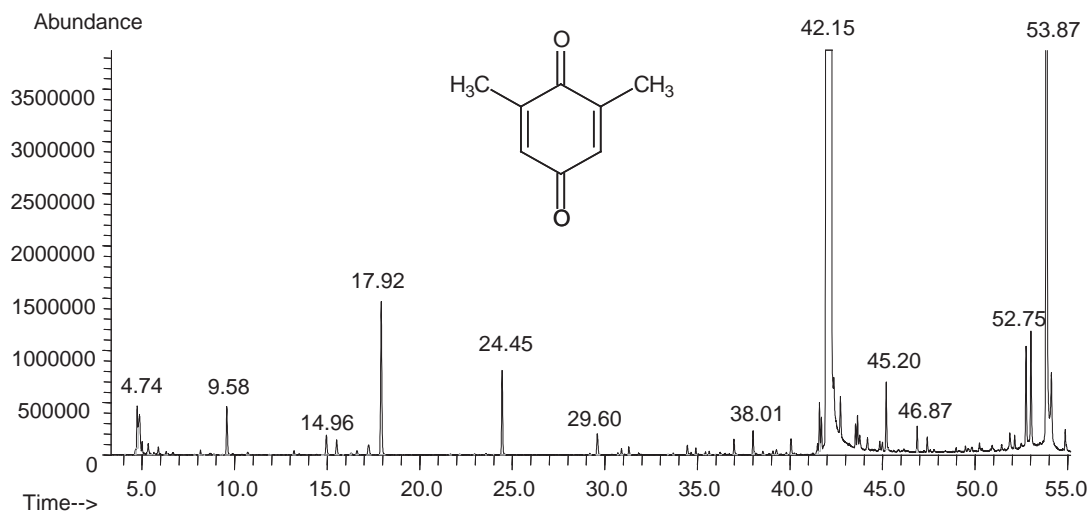


FIGURE 15.2.2. Pyrogram of 2,6-dimethyl-1,4-benzoquinone at 1100°C.

TABLE 15.2.3. Identification of the main peaks in the chromatogram shown in Figure 15.2.2 for the pyrolysis of 2,6-dimethylbenzoquinone at 1100°C (hydrogen, CO, methane, ethane, and water not included)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Carbon dioxide	4.74	44	124-38-9	4.97
2	1,3-Cyclopentadiene	9.59	66	542-92-7	2.23
3	1-Methylcyclopentadiene	14.96	80	96-39-9	0.88
4	1,3-Cyclohexadiene	15.52	80	592-57-4	0.66
5	Benzene	17.92	78	71-43-2	6.70
6	Toluene	24.45	92	108-88-3	2.62
7	<i>p</i> -Xylene	29.60	106	95-47-6	0.69
8	3,4-Bis(methylene)cyclopentanone	36.99	108	27646-73-7	0.44
9	Indene	38.01	116	95-13-6	0.56
10	Phenol	40.07	94	108-95-2	0.52
11	2,5-Dimethyl-2,5-cyclohexadiene-1,4-dione	41.60	136	137-18-8	0.98
12	2-Methylphenol	41.71	108	95-48-7	0.88
13	2,6-Dimethyl-1,4-benzoquinone	42.22	108	527-61-7	Not included
14	3,5-Dimethylphenol	42.37	122	108-68-9	3.75
15	3-Methylphenol	42.73	108	108-39-4	2.37
16	4-Hydroxy-2,4,5-trimethyl-2,5-cyclohexadien-1-one	43.55	152	14353-72-1	0.26
17	Naphthalene	43.65	128	91-20-3	0.50
18	2,4-Dimethylphenol	44.19	122	105-67-9	0.34
19	3,4-Dimethylphenol	45.20	122	95-65-8	1.58
20	1-Methylnaphthalene	46.87	142	90-12-0	0.44
21	2-Methylnaphthalene	47.42	142	91-57-6	0.27
22	Resorcinol	51.88	110	108-46-3	0.64
23	Acenaphthylene	52.14	152	208-96-8	0.25
24	2-Methyl-5-hydroxybenzofuran	52.75	148	6769-56-8	1.95
25	2-Methyl-1,4-benzenediol	53.02	124	95-71-6	2.61

TABLE 15.2.3. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
26	2,6-Dimethyl-1,4-benzenediol	53.87	138	654-42-2	<b>59.82</b>
27	2,5-Dimethyl-1,4-benzenediol	54.13	138	1321-28-4	2.65
28	5-Hydroxy-4-methylindan-1-one	54.87	162	N/A	0.43

Note: Numbers in bold indicate the major pyrolysis constituents

temperature for the generation of ketene is around 635 °C, when only part of the diketone is decomposed. At higher temperatures, the ketene itself is decomposed (see Section 15.3).

Diketones with the two CO groups separated by more carbon atoms typically show less interaction between these groups, and the thermal decomposition is influenced independently by each group. However, a ketone such as 1,4-diphenylbutane-1,4-dione heated for 18 h at 310 °C generates 2,5-diphenylfuran [35].

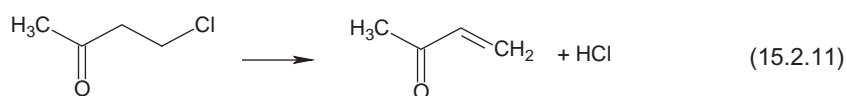
A special group of diketones is the quinones. *p*-Benzoquinone (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>) or cyclohexa-2,5-diene-1,4-dione and its homologs do not have an aromatic character. These compounds are very stable to heating. The decomposition begins to be noticed above 750 °C, but stronger decomposition can be achieved only at higher temperatures. *p*-Benzoquinone is also volatile, and pyrolysis in a pyrolyzer used for solid samples leads to the volatilization of a large amount of compound before reaching the decomposition temperature. The main pyrolysis products of benzoquinone above 900 °C are CO<sub>2</sub>, hydroquinone, and char, with low levels of phenol and traces of benzene, toluene, and naphthalene. The formation of hydroquinone in the thermal decomposition is explained by the high thermal stability of the aromatic ring and the oxidative character of benzoquinone.

2,6-Dimethyl-1,4-benzoquinone decomposes similarly to benzoquinone. The main decomposition product in this case is 2,6-dimethylhydroquinone (2,6-dimethyl-1,4-benzenediol). The pyrolysis of a 0.6-mg sample of 2,6-dimethylbenzoquinone leads to the pyrogram shown in Figure 15.2.2. The pyrolysis was performed using Type 1 Experiment as described in Section 4.6,  $T_{eq} = 1100$  °C,  $\beta = 20$  °C/ms, THT = 10 s, and a housing temperature of  $T_{hou} = 280$  °C. The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications in the pyrogram and their relative molar content in 100 moles of pyrolysate are given in Table 15.2.3. The calculation of the mole percent was obtained based solely on peak areas.

In addition to the compounds listed in Table 15.2.3, the pyrolysis generates a certain amount of char. The presence of naphthalene and acenaphthylene in detectable amounts by direct GC/MS analysis indicates that other PAHs are likely to be in the pyrolysate but at levels below the detection capability of the technique used for the analysis.

### Ketones containing other functional groups

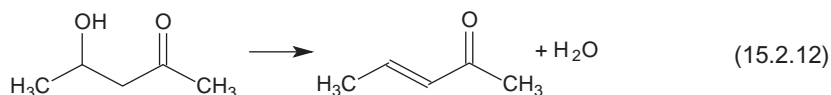
Numerous compounds contain ketone groups in addition to other functional groups. These may include halogen, alcohol, ether, and other groups. In some reactions, the other functional group may be eliminated before the carbonyl group is affected. For example, pyrolysis of phenyl 2,4,6-tribromophenyl ketone (tribromobenzophenone) pyrolyzed around 500 °C generates 1,3-dibromofluoren-9-one, and eliminates HBr. The same elimination of the halogen is seen, for example, during the pyrolysis of 4-chlorobutanone, which takes place by the following reaction:



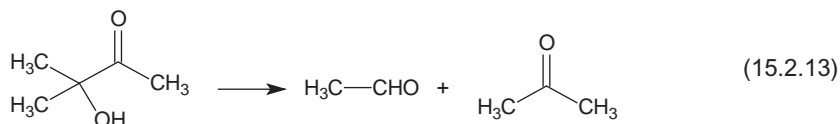
The kinetic parameters for reaction 15.2.11 were determined in the temperature range of 402–424.4 °C and found to follow the Arrhenius equation  $\log k \text{ (s}^{-1}\text{)} = (13.67 \pm 0.69) - (225.2 \pm 8.6) \text{ kJ/mol} / 2.303RT$  [36].

Another common additional group to carbonyl is hydroxyl. The OH group relative to the C=O group can be in vicinal positions ( $\alpha$ -hydroxy ketones) or separated by one ( $\beta$ -hydroxy ketones) or more carbon atoms. Acetol (3-hydroxy-2-butanone) is the simplest hydroxy ketone, and the OH group is in  $\alpha$ -position to the carbonyl. Pyrolysis of this compound around 450 °C generates acetaldehyde and formaldehyde, as well as low levels of CO, H<sub>2</sub>, CH<sub>4</sub>, and crotonaldehyde. Another common  $\alpha$ -hydroxy ketone is benzoin (2-hydroxy-1,2-diphenylethan-1-one). This compound decomposes above 300 °C with the formation of benzyl phenyl ketone (deoxybenzoin), 1,2-diphenylethane-1,2-dione (dibenzoyl), and 1,2-diphenylethane-1-ol [37].

$\beta$ -Hydroxy ketones are somewhat more stable than  $\beta$ -hydroxyaldehydes (aldols), but they decompose in the same manner with elimination of water upon heating at temperatures above 250–300 °C. For example, 4-hydroxypentan-2-one changes at temperatures higher than 250 °C into 3-penten-2-one.



Decomposition of 3-hydroxy-3-methyl-2-butanone at temperatures around 600 K leads to the formation of acetaldehyde and acetone, as shown below:

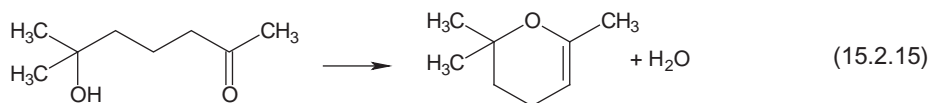


The Arrhenius equation describing reaction 15.2.13 is given by the formula [38]:

$$\log_{10} k \text{ (s}^{-1}\text{)} = 12.4 - \frac{53060}{4.574 T} \quad (15.2.14)$$

Decomposition of hydroxy ketones with the OH group at carbon atoms situated farther from the carbonyl group starts to show similarities with the decomposition of carbohydrates, the water elimination remaining a major reaction under the influence of heat.

The formation of stable heterocycles is sometimes the reason why the pyrolysis of some compounds takes a specific path. For example, 6-hydroxy-6-methylheptan-2-one decomposes upon distillation in vacuum around 125 °C to form 2,2,6-trimethyl-2H-3,4-dihydropyran, as shown in the following reaction [18]:

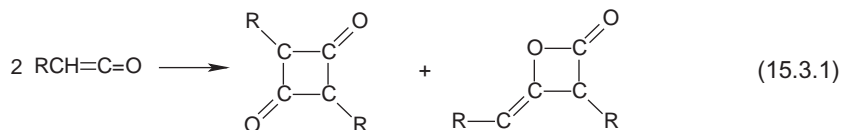


### 15.3. KETENES

#### General aspects

Ketenes are carbonyl compounds containing the CO group connected by a double bond to a carbon atom. Ketenes have the general formula  $\text{RR}'\text{C}=\text{CO}$ , where R and R' are hydrocarbon radicals. The simplest ketene ( $\text{CH}_2=\text{C}=\text{O}$ , ethenone) is also named just ketene. Ketenes are reactive compounds that dimerize to diketenes. Some ketenes such as ethenone dimerize forming a lactone (oxetan-2-one). Methyl ketene generates two dimers, one with a lactone structure and the other having a

cyclobutandione structure. The formation of the two possible dimers is shown in the following reaction:



Ketene (ethenone) is present mainly as a lactone. Ketenes and ketene dimers have various practical applications such as paper sizing.

### Ketene (ethenone)

The study of ketene pyrolysis is related particularly with the pyrolysis of acetone [28] and with combustion of different fuels [39,40], particularly of acetylene [41]. Pyrolysis results generated using shock tube experiments were reported for ketene pyrolysis [42], as well as oxidation [43]. The study for pyrolysis was performed on mixtures containing 0.26% and 2.2% ketene diluted with argon in the temperature range 1102–1921 K. The main pyrolysis products were CO, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub>. The reaction times varied between 1.7 ms and 2.1 ms. The variation of the ratio C/C<sub>0</sub> of the concentration of the reaction product (C) vs. initial ketene concentration (C<sub>0</sub>) as a function of temperature is shown in Figure 15.3.1 [42].

The whole process was modeled with a computer simulation using 38 elementary reactions [42]. The ketene consumption took place following seven reactions. The experimental and calculated values for *A*, *n*, and *E*<sup>‡</sup> in Arrhenius equation  $k = A T^n \exp(-E^\ddagger/RT)$  as well as the heats of reaction  $\Delta H^\circ$  (kcal/mol) for these reactions are given in Table 15.3.1.

The oxidation of ketene was evaluated in several gas mixtures containing between 0.26% and 2.26% acetone, oxygen, or N<sub>2</sub>O as oxidant from 0.14% to 2%, all diluted to 100% with argon [43]. The temperature range for the study was between 1050 K and 2050 K. The main reaction product during oxidation was CO. Lower levels of CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and CH<sub>4</sub> were also generated. The initiation is probably controlled by the formation of free O<sup>••</sup> atoms and OH<sup>•</sup> free radicals that further react with ketene by reactions as shown below:

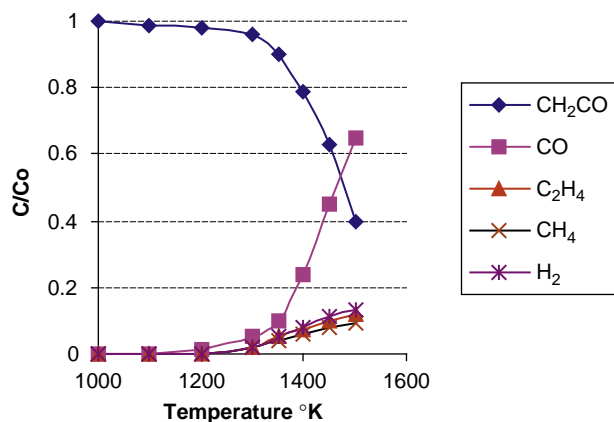
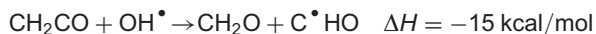
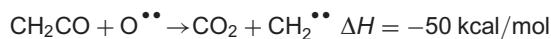
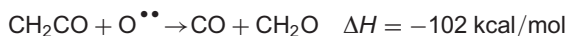


FIGURE 15.3.1. Variation of C/C<sub>0</sub> as a function of temperature for ketene (initial concentration C<sub>0</sub>) and some ketene pyrolysis products [42].



TABLE 15.3.1. The values for the frequency factor  $A$  (per second), temperature exponent  $n$ , and activation energy  $E$  (cal/mol) in Arrhenius equation and for the heats of formation (kcal/mol) for the main reactions responsible for ketene consumption [42]

No.	Reaction	$A$ ( $s^{-1}$ )	$n$	$E^\ddagger$ (cal/mol)	$\Delta H^\circ$ (kcal/mol)
1	$CH_2CO + M \rightarrow CH_2^{\bullet\bullet} + CO + M$	$3.96 \times 10^{15}$	0	59300	+75.8
2	$CH_2CO + H^\bullet \rightarrow CH_3^\bullet + CO$	$1.11 \times 10^7$	2	2000	-32.5
3	$CH_2CO + H^\bullet \rightarrow CHCO^\bullet + H_2$	$1.80 \times 10^{14}$	0	8600	-0.7
4	$CH_2CO + CH_2^{\bullet\bullet} \rightarrow C_2H_4 + CH_3^\bullet$	$1.00 \times 10^{12}$	0	0	-94.2
5	$CH_2CO + CH_2^{\bullet\bullet} \rightarrow CHCO^\bullet + CH_3^\bullet$	$3.60 \times 10^{13}$	0	11000	-4.3
6	$CH_2CO + CH_3^\bullet \rightarrow C_2H_5^\bullet + CO$	$9.00 \times 10^{10}$	0	0	-23.0
7	$CH_2CO + CH_3^\bullet \rightarrow CHCO^\bullet + CH_4$	$7.50 \times 10^{12}$	0	13000	+0.7

A computer simulation using 85 reactions with rate constants available in the literature or generated during the study was performed to explain the experimental data obtained from ketene oxidation [43].

### Other ketenes

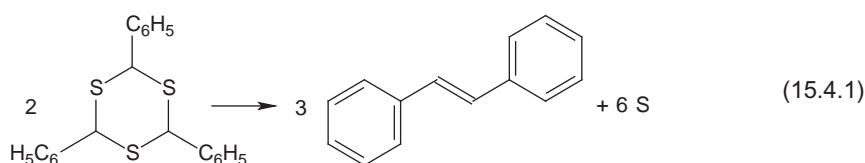
Besides pyrolysis of ethenone (ketene), several studies on other ketenes and ketene dimers were performed [44,45]. One of these studies evaluated thermal decomposition of dichloroketene [45]. This compound decomposes similarly to ketene, the main initiation reaction being the formation of  $CCl_2^{\bullet\bullet}$  and CO. Another study was directed toward pyrolysis of the dimers of ketenes with tetradecyl, hexadecyl, and octadecyl substituents [44].

## 15.4. THIOALDEHYDES AND THIOKETONES

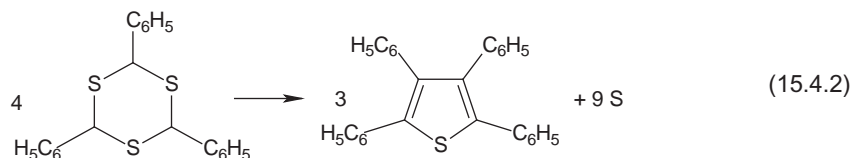
### General aspects

The replacement of the oxygen atom in the formula of an aldehyde or ketone with a sulfur atom leads to the formation of thioaldehydes and thioketones, respectively. (Experimentally, these compounds can be obtained from the aldehydes and ketones by saturating their alcoholic solutions with  $H_2S$  in the presence of a hydracid such as HCl.) Aliphatic thioaldehydes and thioketones have a strong tendency to polymerize, and their isolation is problematic. Aromatic thioaldehydes and thioketones with at least one aromatic substituent are more stable. However, these compounds still have the tendency to polymerize, for example, with the formation of trimers (in a reaction similar to the formation of *para*acetaldehyde from acetaldehyde).

Pyrolysis of thioaldehydes and thioketones does not show much similarity with that of typical aldehydes and ketones, since they have the tendency to generate sulfur upon pyrolysis. For example, trithiobenzaldehyde around 190 °C decomposes as shown in the following reaction:



The tendency to produce stable heterocycles is seen at higher temperatures, when trithiobenzaldehyde generates tetraphenylthiophene:



Aromatic or partly aromatic thioketone trimers such as trithioacetophenone generate the monomers by distillation. Upon heating at the boiling point for longer periods of time, the decomposition takes place with the formation of styrene, ethylbenzene, diphenylthiophene, and sulfur. Thiobenzophenone decomposes at the distillation temperature generating tetraphenylethylene, sulfur,  $\text{H}_2\text{S}$ , and char [46].

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## CHAPTER 16

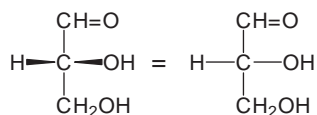
*Pyrolysis of Carbohydrates***16.1. MONOSACCHARIDES*****General aspects***

In nature, the most abundant class of biomolecules is that of carbohydrates, including compounds from plants (glucose, fructose, cellulose, starch, pectin, etc.), animals (glucose, glycogen, etc.), bacteria, fungi, archaea, and protists (microbial and fungal polysaccharides, etc.). Carbohydrates (saccharides or sugars) are organic compounds containing in their molecule one or more carbonyl groups and two or more alcohol groups on an aliphatic hydrocarbon chain. These compounds can be classified as monosaccharides, oligosaccharides, and polysaccharides.

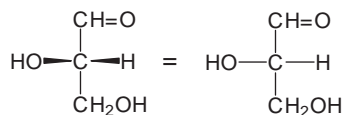
The general formula for monosaccharides is  $C_nH_{2n}O_n$  ( $n = 3$  for trioses,  $n = 4$  for tetroses,  $n = 5$  for pentoses, etc.). The oligosaccharides and polysaccharides are generated by the elimination of water from two or more monosaccharide molecules, the sugar units being connected by an ether group. Besides simple carbohydrates that contain only carbonyl and alcohol functional groups (as well as ether for oligosaccharides and polysaccharides), more complex carbohydrates also are known. These may include other functional groups such as halogen, carboxyl ( $-\text{COOH}$ ), amino ( $-\text{NH}_2$ ), amido ( $-\text{NHCO}-\text{R}$ ) etc. Several deoxy sugars (with the hydroxyl group replaced by hydrogen) are also known (e.g., deoxyribose, rhamnose, etc.).

Besides natural carbohydrates, many synthetic carbohydrates were produced. Some are related to chemically modified polysaccharides (e.g., ethyl cellulose, carboxymethyl cellulose). Others are synthetic small organic molecules.

Glyceraldehyde and dihydroxyacetone ( $n = 3$ ) can be considered the simplest monosaccharides. Glycolaldehyde or hydroxyacetaldehyde  $\text{HOCH}_2-\text{CHO}$  also is considered by some a two-carbon monosaccharide. Glyceraldehyde has one asymmetric carbon. Consequently, for this compound there are two possible enantiomers R (or D) and S (or L) (the R form is shown with the OH to the right of the carbon chain, and the S form with the OH to the left):



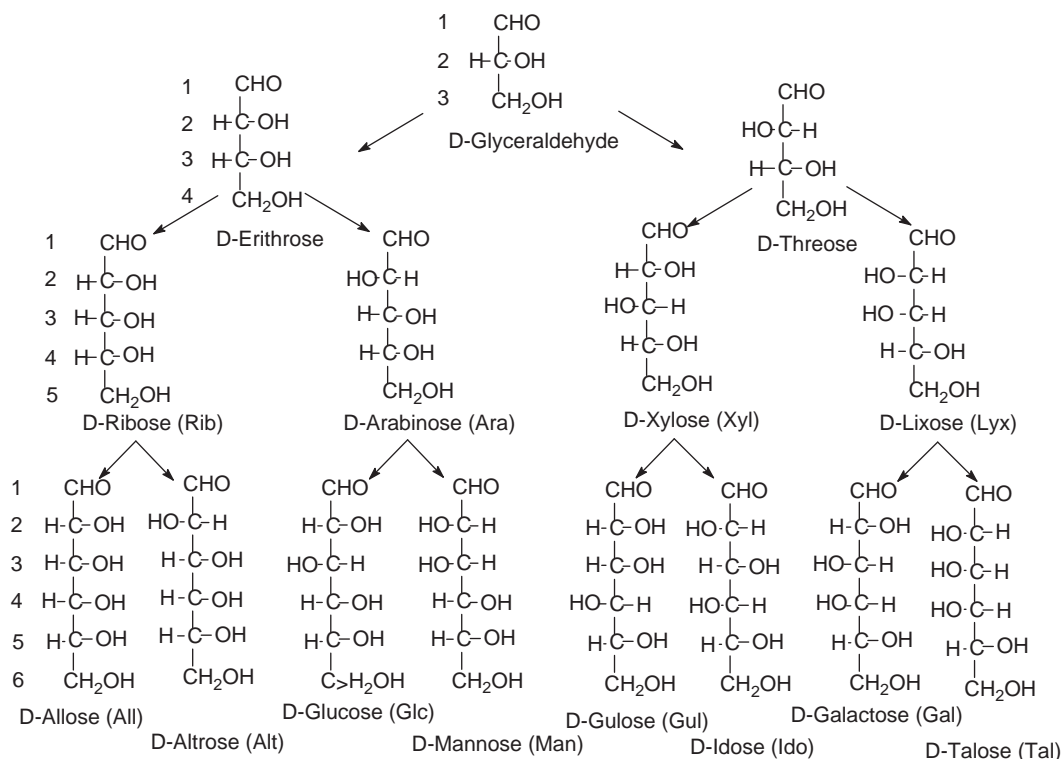
D-Glyceraldehyde



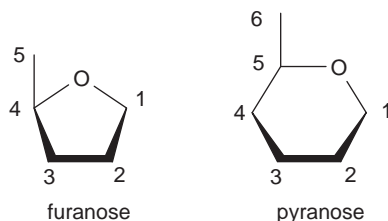
L-Glyceraldehyde

All monosaccharides with a larger number of carbons can be conventionally derived from glyceraldehyde or dihydroxyacetone by including more  $\text{H}-\text{C}-\text{OH}$  units in the carbon chain. Glyceraldehyde leads to the series of aldoses, and dihydroxyacetone to the series of ketoses. The aldoses with the same stereochemistry as D-glyceraldehyde at the asymmetric carbon that is the most distant from the carbonyl group will form the D-series of aldoses. The monosaccharides with the same stereochemistry

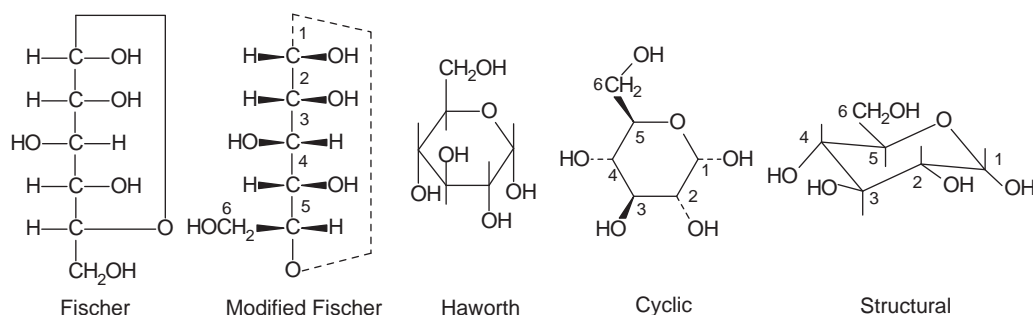
as L-glyceraldehyde at the most distant asymmetric carbon will form the L-series. The D-series of aldoses is shown below:



In monosaccharides with  $n > 4$ , it is common that the carbonyl group forms with one of the  $-OH$  groups an internal hemiacetal, such that many monosaccharides have a cyclic structure. The open chain (linear) form of monosaccharides with  $n > 4$  can be found only in water solutions as a small proportion of the dissolved compound. The cyclic hemiacetal can have the form of a five-atom ring (furanose) or of a six-atom ring (pyranose). The proportion of furanose form vs. pyranose form at equilibrium depends on the structure of the sugar. Glucose, for example, is present almost completely in pyranose form, while talose is about 69% pyranose and 31% furanose. The formation of the cyclic hemiacetals of monosaccharides adds one more asymmetric carbon to their structure, compared to the linear form. For example, linear glucose has four asymmetric carbons, while cyclic glucose has five asymmetric carbons. The new asymmetric C-1 has two possible steric forms (two anomers), indicated as  $\alpha$  and  $\beta$ .



The configurations of cyclic monosaccharides are described by several types of formulas. As an example, the following formulas are shown for glucose,  $\alpha$ -D-glucopyranose: Fischer, modified Fischer, Haworth, cyclic, and structural (shorter bonds in the Haworth and structural formulas indicate  $-H$ ).



Fischer formulas have the same orientation of the OH groups as the linear ones. In the Haworth formulas (of aldoses) the side chain (e.g., CH<sub>2</sub>OH group) is up when it is attached to an R carbon (the original OH to this carbon was to the right in the linear formula), and it is down when the carbon to which it is attached in the ring is S. If the side chain is up, the position of the other substituents (e.g., OH) is reversed to what it was in the Fischer formula (see Fischer and modified Fischer formulas for glucose). In this way, the OH groups on the right (R) from Fischer formula (and from the linear form) are down in the Haworth formula. For the side chain down, the OH (and other) groups on the right in Fischer formula are up in the Haworth formula, and those to the left are down. For D-aldoses the steric assignment for the C-1 carbon is  $\alpha$  when this is an S carbon (and it is shown down) and is  $\beta$  when this is an R carbon.

The nomenclature of carbohydrates includes common names as well as systematic names. The common names are sometimes indicated by a three-letter convention, arabinose (Ara), glucose (Glc), galactose (Gal), etc. The IUPAC name of carbohydrates can be found in the literature [1]. In IUPAC nomenclature, the numbering of atoms includes not only the carbons but also the oxygen atom (which is numbered as 1). For this reason, the IUPAC name of  $\alpha$ -D-glucopyranose is (2S,3R,4S,5R,6R)-6-(hydroxymethyl)tetrahydro-2H-pyran-2,3,4,5-tetraol.

Monosaccharides and the lower oligosaccharides (e.g., di-, trisaccharides), being small organic molecules, are included among the molecules further discussed in this chapter regarding their thermal decomposition. The presentation of pyrolysis of polysaccharides (such as cellulose, starch, chitin, etc.) is beyond the purpose of this book and can be found in various other publications (see e.g., [2]). The importance of studying the pyrolysis of carbohydrates is related to the wide distribution in nature of this class of compounds. Pyrolysis can occur in a variety of intentional and unintentional processes such as pyrolysis in incinerators, forest fires, cigarette smoking, and food cooking [3].

### Monosaccharides with less than six carbon atoms

There is very little direct information regarding the pyrolysis of trioses and tetroses. Under initial mild heating, condensation of these molecules takes place, and further pyrolysis generates compounds similar to those of higher sugars. In basic conditions and heating (e.g., in the presence of NaOH or by treatment with tetramethylammonium hydroxide, TMAH) these compounds generate carboxylic acids (formic, acetic), hydroxycarboxylic acids (glycolic, lactic), and various lactones [4,5].

Pentoses' pyrolysis has been more frequently reported in the literature [5–8]. The pyrolysis of these compounds at temperatures higher than 550 °C typically generates as the main products H<sub>2</sub>O, CO<sub>2</sub>, aldehydes (hydroxyacetaldehyde, formaldehyde, acetaldehyde, etc.), ketones (butanone, 1-hydroxypropanone, etc.), furan and pyran derivatives (high levels of furfural), as well as several deoxy sugars. Smaller molecules that do not have chiral centers and are generated during pyrolysis are very similar for different pentoses. As an example, the time window between start and 41 min of the pyrograms for D-(–)-arabinose, D-(–)-ribose, and D-(+)-xylose is shown in Figure 16.1.1. Arabinose and ribose are present mainly in furanose form, while xylose is mainly present in pyranose form.

Pyrolysis of all samples shown in Figure 16.1.1 was performed on 1.0 mg compound using Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900$  °C,  $\beta = 10$  °C/ms, THT = 10 s, and housing

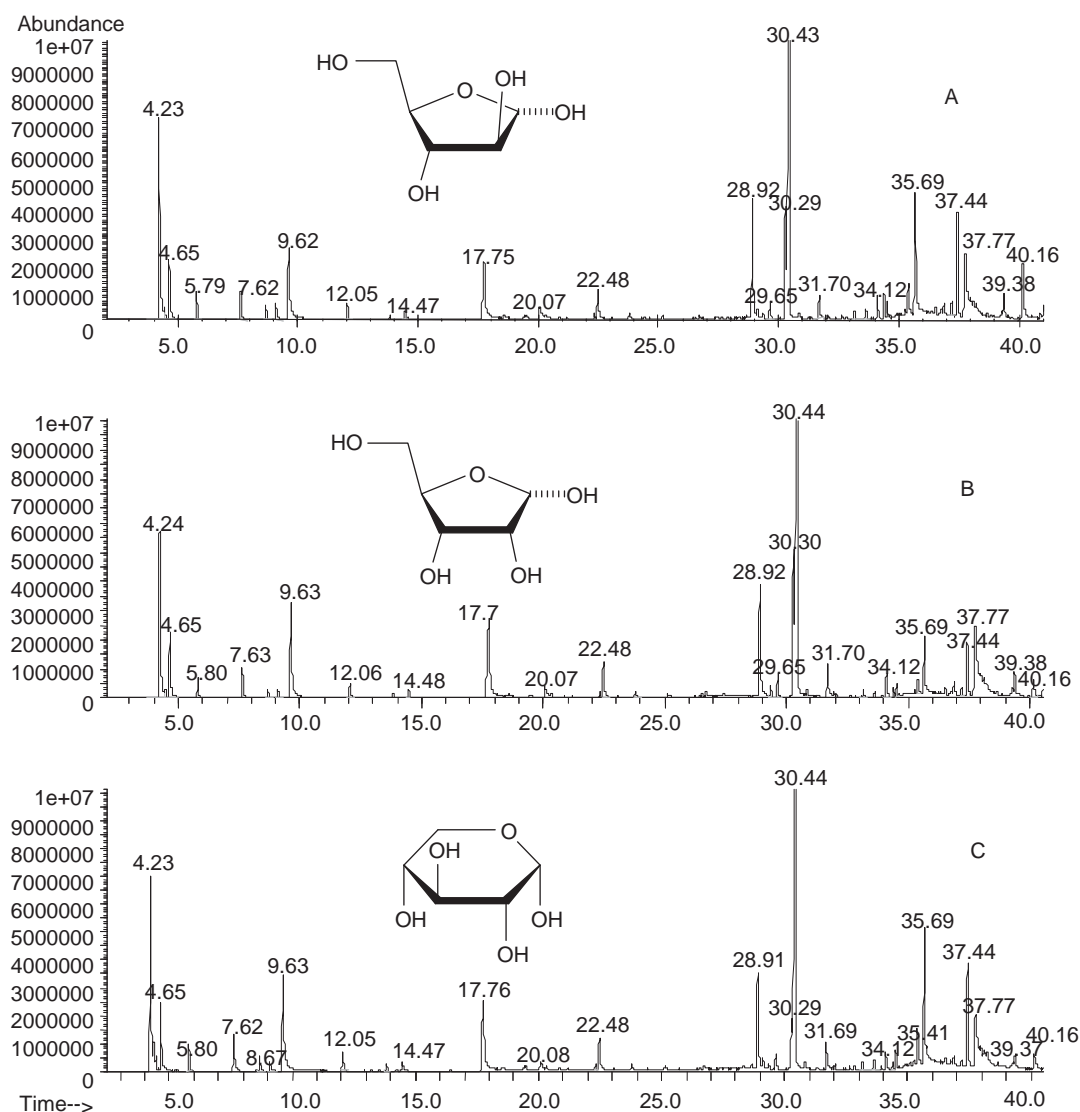


FIGURE 16.1.1. First 41 min from the pyrograms obtained at 900 °C from 1.0 mg D-(-)-arabinose (Trace A), D-(-)-ribose (Trace B), and D-(+)-xylose (Trace C).

temperature  $T_{\text{hou}} = 280\text{ }^{\circ}\text{C}$ . The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications and their relative molar content in 100 moles of mixture that includes only the compounds eluting in the first 41 min in the pyrogram are shown in Table 16.1.1. In addition, the calculation of the mole percent was obtained solely based on peak areas, and since differences in the MS response factors can be quite large for different compounds, the estimations may have large errors.

As shown in Table 16.1.1, for the compounds generated by pyrolysis and eluting from the chromatographic column in the first 41 min, both the nature and the relative concentration of the compounds generated from the three analyzed pentoses is very similar, in spite of the difference in the cycle type (furanose or pyranose) assumed by the sugar.

At longer retention times in the pyrograms, several heavier and more polar compounds start eluting. Figure 16.1.2 displays the time window from 42 min to 58 min for the pyrograms of 1.0 mg

TABLE 16.1.1. Identification of the main peaks in the chromatograms shown in Figure 16.1.1A, 16.1.1B, and 16.1.1C for pyrolysis at 900°C of D-(–)-arabinose (Trace A), D-(–)-ribose (Trace B), and D-(+)-xylose (Trace C)

No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent (for compounds eluting in the first 42 min)		
					Arabinose	Ribose	Xylose
1	Carbon dioxide	4.24	44	124-38-9	14.25	11.36	11.14
2	Propene	4.47	42	115-07-1	0.83	0.67	0.86
3	Formaldehyde	4.65	30	50-00-0	6.20	6.50	6.53
4	Acetaldehyde	5.81	44	75-07-0	1.61	1.17	1.38
5	Furan	7.63	68	110-00-9	1.32	1.42	1.31
6	2-Propenal	8.69	56	107-02-8	0.76	0.45	0.85
7	Acetone	9.10	58	67-64-1	1.14	0.50	0.63
8	Pyruvaldehyde	9.63	72	78-98-8	4.29	5.17	5.43
9	2-Methylfuran	12.06	82	534-22-5	0.73	0.59	0.82
10	Butenal	13.85	72	123-72-8	0.20	0.21	0.28
11	2,3-Butanedione	14.48	86	431-03-8	0.31	0.34	0.33
12	Hydroxyacetaldehyde	17.77	60	141-46-8	5.74	8.52	6.72
13	Formic acid	18.50	46	64-18-6	0.23	0.23	0.13
14	Acetic acid	20.07	60	64-19-7	0.84	0.88	0.67
15	Ethyl-1-propenyl ether	22.33	86	928-55-2	0.15	0.15	0.18
16	1-Hydroxy-2-propanone	22.48	74	116-09-6	1.39	1.60	1.48
17	Toluene	23.07	92	108-88-3	0.09	0.09	0.06
18	Methyl formate?	23.80	60	107-31-3	0.43	0.44	0.25
19	Hydroxyacetic acid (glycolic acid)	24.63	76	79-14-1	0.08	0.08	trace
20	2,2'-Bioxirane?	26.71	86	1464-53-5	0.04	0.07	0.02
21	1,4-Dioxadiene	28.92	84	N/A	4.44	4.27	3.49
22	3-Furaldehyde	29.13	96	498-60-2	0.27	0.04	0.32
23	2-Oxopropionic acid methyl ester	29.36	102	600-22-6	0.12	0.34	0.12
24	2,5-Furandione	29.65	98	108-31-6	0.51	0.63	0.45
25	2-Cyclopentene-1,4-dione	30.30	96	930-60-9	3.43	4.60	1.37
26	Furancarboxaldehyde (furfural)	30.44	96	98-01-1	26.22	30.62	32.24
27	2-Propylfuran	30.83	110	4229-91-8	Trace	0.08	0.31
28	2-Furanmethanol	31.70	98	98-00-0	0.76	1.03	0.85
29	1-(2-furanyl)ethanone	33.16	110	1192-62-7	0.22	0.24	0.23
30	5,6-Dihydro-2H-pyran-2-one	33.65	98	3393-45-1	0.38	Trace	0.39
31	2-Methylcyclopentene-1-one	33.93	96	1120-73-6	0.02	0.06	0.02
32	Dihydro-4-hydroxy-2(3H)-furanone	34.12	102	5469-16-9	0.74	0.74	0.60
33	Dihydro-3-methylene-2(3H)-furanone	34.40	98	547-65-9	0.64	0.24	0.21
34	2-Hydroxy-2-cyclopenten-1-one	34.53	98	10493-98-8	0.41	0.33	0.46
35	2-Methylenecyclopentanol	35.41	98	20461-31-8	1.12	0.54	1.28
36	2,3-Dihydroxypropanal	35.67	90	367-47-5	5.28	2.41	6.45
37	Butyrolactone	36.54	86	96-48-0	0.42	0.17	0.53

(Continued)



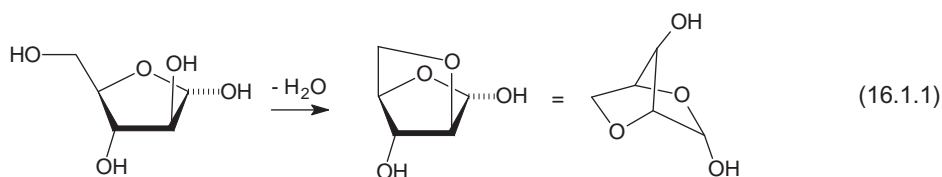
TABLE 16.1.1. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent (for compounds eluting in the first 42 min)		
					Arabinose	Ribose	Xylose
38	Tetrahydro-4H-pyran-4-one	36.77	100	29943-42-8	0.34	0.12	0.33
39	5-Methyl-2,3-dihydrofuran-2,4-dione	36.89	114	N/A	0.50	0.44	0.39
40	Ethyl-1-propenyl ether?	37.20	86	928-55-2	0.47	0.23	0.21
41	6,8-Dioxabicyclo[3.2.1]octane	37.44	114	280-16-0	2.45	1.38	2.58
42	1,3-Dihydroxy-2-propanone	37.77	90	96-26-4	4.59	5.25	3.91
43	2-Hydroxy-3-methyl-2-cyclopenten-1-one	37.99	112	80-71-7	0.81	0.79	0.81
44	2H-Pyran-2,6(3H)-dione	38.13	112	5926-95-4	0.62	1.43	0.61
45	4,5-Dimethyl-1,3-dioxol-2-one?	39.38	114	37830-90-3	0.78	0.72	0.44
46	Unknown	40.16	114	N/A	1.94	0.66	0.58
47	3-Furancarboxylic acid methyl ester	40.88	126	13129-23-2	0.20	0.20	0.19
48	Unknown	41.03	116	N/A	0.32	0.33	0.14
49	Unknown	41.29	130	N/A	0.61	0.62	0.65
50	Unknown	40.55	98	N/A	0.06	0.24	0.02
51	3-Furancarboxylic acid methyl ester	40.88	126	13129-23-2	0.10	0.19	0.18
52	Unknown	41.29	130	N/A	0.61	0.62	0.60

Hydrogen, CO, methane, ethane, and water not included.

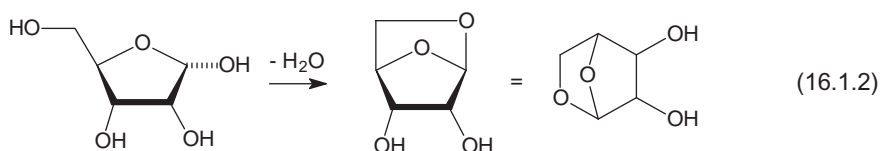
D-(–)-arabinose (Trace A), D-(–)-ribose (Trace B), and D-(+)-xylose (Trace C) (the first part of these chromatograms is shown in Figure 16.1.1).

The correct identity of the peaks from these time windows in the pyrograms was more difficult to obtain through searches in the available mass spectral libraries. The peak eluting at 43.15 min in the three pyrograms was tentatively identified as resulting from the molecules of pentoses by the elimination of two water molecules to generate a 5,7-dioxabicyclo[2.2.1]heptenol. Several isomers and diastereoisomers of this compound are possible. The peak at 45.51 min for xylose was tentatively identified as tetrahydro-3,4-furandiol (available in the mass spectral libraries). The peak at 45.56 min for arabinose and at 45.51 min for ribose is not pure, being formed from tetrahydro-3,4-furandiol mixed with 2,5-anhydro-arabinofuranose (3,6-dioxabicyclo[2.2.1]heptane-2,7-diol) and 2,5-ribofuranose, respectively. The reaction of the formation of 2,5-anhydro-arabinofuranose is shown below:



The mass spectrum of 3,6-dioxabicyclo[2.2.1]heptane-2,7-diol is shown in Figure 16.1.3. This compound is not formed from xylose.

By the loss of one water molecule, all three sugars form 5,7-dioxabicyclo[2.2.1]heptane-2,3-diols in reactions shown below for ribose and for xylose.



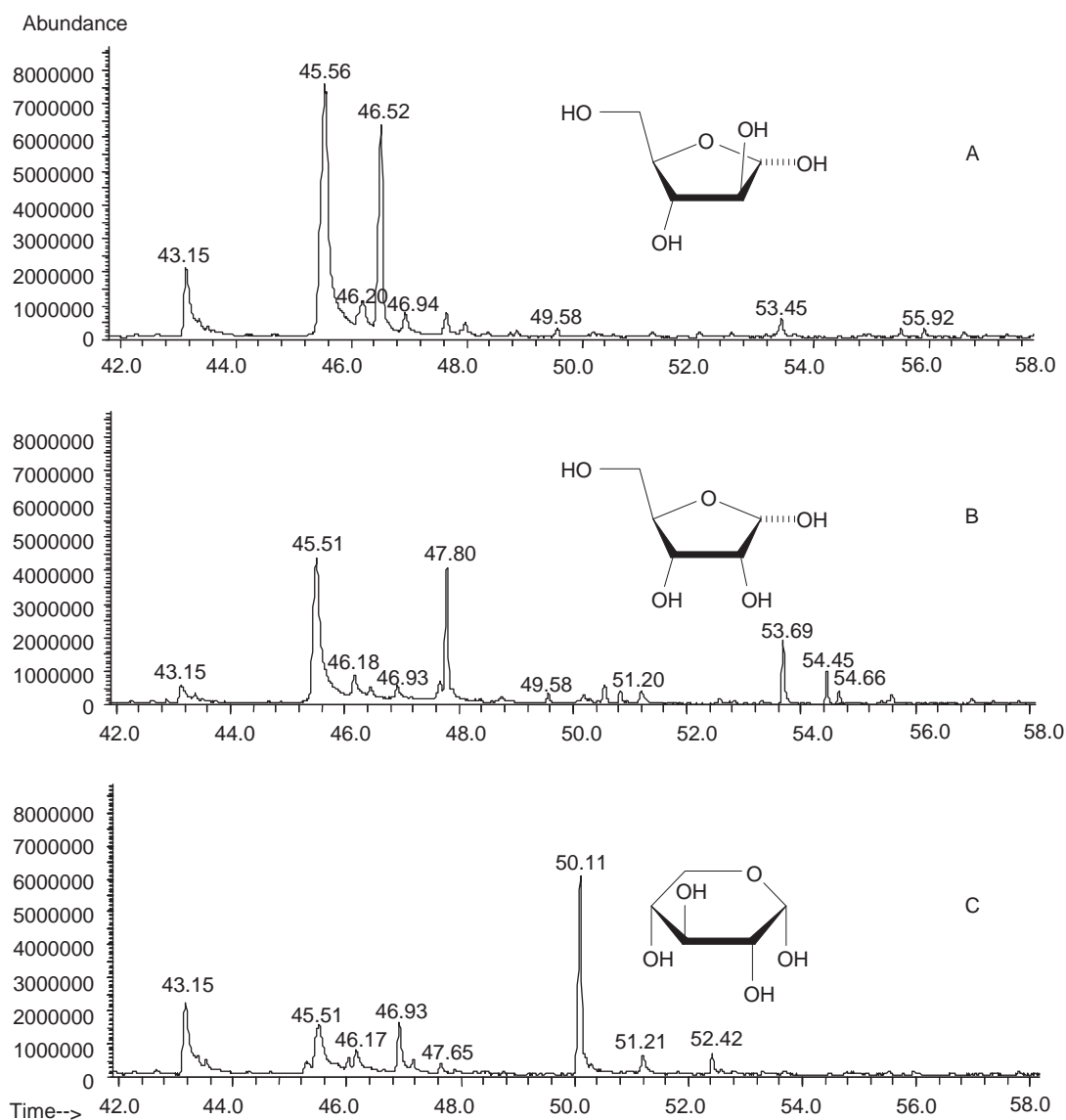
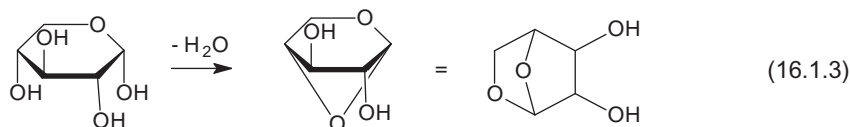


FIGURE 16.1.2. Time window between 42 min and 58 min from the pyrograms obtained at 900 °C from 1.0 mg *D*-(-)-arabinose (Trace A), *D*-(-)-ribose (Trace B), and *D*-(+)-xylose (Trace C).



5,7-Dioxabicyclo[2.2.1]heptane-2,3-diol has four chiral centers (and therefore potentially 16 stereoisomers). The stereoisomers of this compound contain part of the chiral centers of the initial molecule and can be indicated as 1,5-anhydro-arabinose when generated from arabinose, and 1,5-anhydro-ribose when generated from ribose, etc. The diastereoisomers can be separated on non-chiral chromatographic columns, and their mass spectra are identical (or very similar). The diastereoisomer from arabinose elutes at 46.52 min, the one from ribose at 47.8 min, and the one from xylose at 50.11 min. The spectrum of 5,7-dioxabicyclo[2.2.1]heptane-2,3-diol (1,4-anhydro-xylopyranose) obtained from xylose is shown in Figure 16.1.4. The spectra of 1,5-anhydro-arabinofuranose and

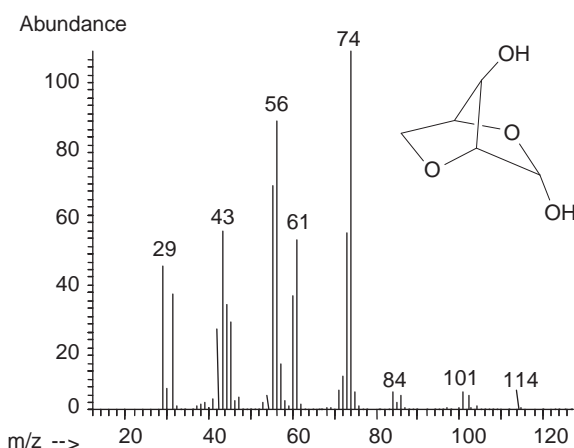


FIGURE 16.1.3. Mass spectrum of 3,6-dioxabicyclo[2.2.1]heptane-2,7-diol obtained from arabinose.

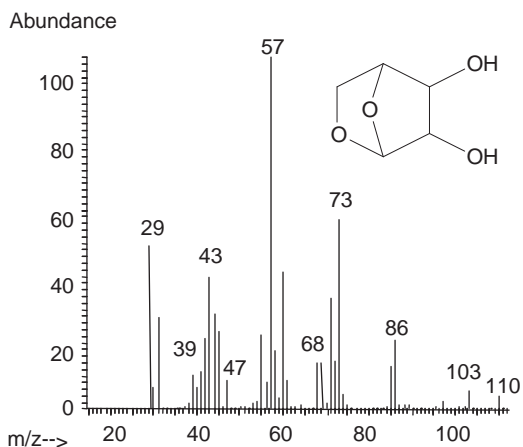


FIGURE 16.1.4. Mass spectrum of 5,7-dioxabicyclo[2.2.1]heptane-2,3-diol obtained from xylose.

1,5- anhydro-ribofuranose are virtually identical with that of 1,4-anhydro-xylopyranose except for the fragment  $m/z = 110$ , which is absent in these spectra.

Pentoses pyrolysate contains a number of compounds with more than two OH groups, and some of these compounds may not elute from the chromatographic column when conditions given in Table 4.6.1 are used. For this reason, a second experiment was performed by pyrolyzing 1.0 mg of the sugars at 900 °C followed by collection of the pyrolysate and derivatization with bis(trimethylsilyl)trifluoroacetamide (BSTFA) in conditions described in Section 4.6. The analysis of the derivatized pyrolysate was done with GC/MS technique in conditions described in Table 4.6.2. Besides the compounds already identified in Table 16.1.1, the analysis of the silylated pyrolysate showed the presence of some undecomposed initial sugar. Also, the formation of dimers generated by the elimination of water from two molecules of the initial sugars was detected.

## Glucose

D-(+)-Glucose is probably the most common monosaccharide. The compound is a hexose present mainly in pyranose form, and the ratio of the anomers in solution is 36/64  $\alpha/\beta$ . Glucose decomposition

starts at melting temperature at 153–156 °C with the formation of 1,6-anhydroglucose and of several di- and oligosaccharides [9]. Among the disaccharides (see Section 16.2) detected in glucose heated around the melting temperatures for 2.5 h were 2-O- $\alpha$ -D-glucopyranosyl-D-glucose (kijibiose Glc  $\alpha$ (1 $\rightarrow$ 2) Glc), 2-O- $\beta$ -glucopyranosyl-D-glucose (sophorose Glc  $\beta$ (1 $\rightarrow$ 2) Glc), 3-O- $\alpha$ -D-glucopyranosyl-D-glucose (nigerose Glc  $\alpha$ (1 $\rightarrow$ 3) Glc), 3- $\beta$ -D-glucosyl-D-glucose (laminaribiose Glc  $\beta$ (1 $\rightarrow$ 3) Glc), 4-O- $\alpha$ -D-glucopyranosyl-D-glucose (maltose Glc  $\alpha$ (1 $\rightarrow$ 4) Glc), 4-O- $\beta$ -D-glucopyranosyl-D-glucose (cellobiose Glc  $\beta$ (1 $\rightarrow$ 4) Glc), 6-O- $\alpha$ -D-glucopyranosyl-D-glucose (isomaltose Glc  $\alpha$ (1 $\rightarrow$ 6) Glc), 6-O- $\beta$ -D-glucopyranosyl-D-glucose (gentiobiose Glc  $\beta$ (1 $\rightarrow$ 6) Glc), and  $\alpha$ -D-glucopyranosyl- $\alpha$ -D-glucopyranoside (trehalose Glc  $\alpha$ (1 $\rightarrow$ 1) $\alpha$  Glc) [10]. Among the trisaccharides, were identified (tentatively) maltotriose (Glc  $\alpha$ (1 $\rightarrow$ 4) Glc  $\alpha$ (1 $\rightarrow$ 4) Glc) and panose (Glc  $\alpha$ (1 $\rightarrow$ 6) Glc  $\alpha$ (1 $\rightarrow$ 4) Glc).

At higher temperatures, glucose decomposition generates a large number of molecular fragments [6,11–15]. Pyrolysis of a sample of D-(+)-glucose performed on 1.0 mg compound using Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900$  °C,  $\beta = 10$  °C/ms, THT = 10 s, and housing temperature  $T_{hou} = 280$  °C, generates the pyrogram shown in Figure 16.1.5. Pyrolysis of glucose at temperatures as low as 550 °C generated a pyrogram very similar to that at 900 °C, including the nature of the pyrolytic compounds and the relative peak intensities in the pyrogram. This indicates that for glucose (and other similar carbohydrates) the heating at temperatures beyond the decomposition point brings minor changes in the pyrolysate composition. The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 16.1.2. Since the main pyrolysis products of glucose and fructose are very similar, Table 16.1.2 also contains the identification of the main compounds from the pyrolysis of fructose with the pyrogram shown later in Figure 16.1.13. The calculation of the mole percent was obtained based solely on peak areas.

The correct identification of various compounds in glucose pyrolysis is sometimes a problem. The complexity of pyrolysate mixture as well as variations in the pyrolysis conditions may lead to some variations in the results reported in the literature. For example, besides the compounds listed in Table 16.1.2, a few compounds such as 2-oxopropanal (MW = 72) or 1-hydroxybutane-2,3-dione (MW = 102) were not identified in the pyrogram although reported in the literature [16]. Also the correct identification of anhydro sugars is sometimes a problem, since the corresponding mass spectra are not available in common mass spectral libraries and different anhydro sugars have similar spectra. For comparison, the spectra of 1,6-anhydro- $\beta$ -D-glucopyranose (levoglucosan) and 1,6-anhydro- $\beta$ -D-glucofuranose are shown in Figures 16.1.6 and 16.1.7, respectively.

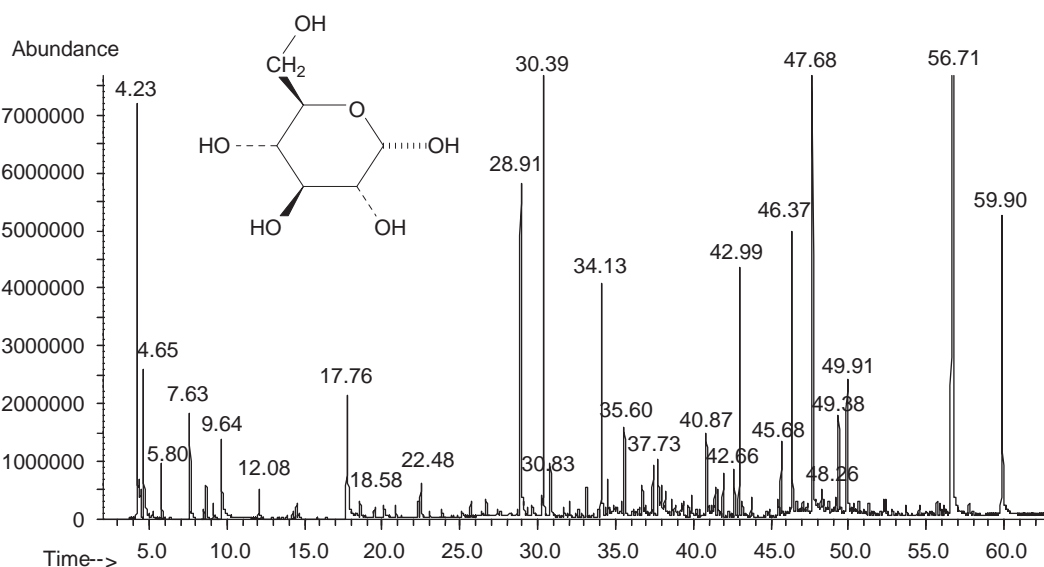


FIGURE 16.1.5. Pyrogram of 1.0 mg D-(+)-glucose at 900 °C. Peak assignment in Table 16.1.2.

TABLE 16.1.2. Identification of the main peaks in the chromatogram shown in Figure 16.1.5 for the pyrolysis of glucose and in Figure 16.1.13 for the pyrolysis of fructose at 900°C

No.	Compound	Ret. time (min)	MW	CAS no.	Glucose moles percent	Fructose moles percent
1	Carbon dioxide	4.23	44	124-38-9	<b>10.37</b>	<b>10.12</b>
2	Formaldehyde	4.65	30	50-00-0	<b>6.73</b>	9.00
3	1-Butene	5.02	56	106-98-9	0.04	Trace
4	1-Butyne	5.21	54	107-00-6	0.04	Trace
5	Acetaldehyde	5.80	44	75-07-0	1.41	0.85
6	Furan	7.63	68	110-00-9	1.69	0.45
7	1,3-Cyclopentadiene	8.53	66	542-92-7	0.20	Trace
8	2-Propenal (acrolein)	8.68	56	107-02-8	0.82	0.44
9	Propanal	8.70	58	123-38-6	0.21	0.11
10	Acetone	9.11	58	67-64-1	0.50	0.70
11	Pyruvaldehyde	9.64	72	78-98-8	2.52	1.86
12	2-Methylfuran	12.08	82	534-22-5	0.57	0.60
13	2-Propen-1-ol	13.55	58	107-18-6	0.04	Trace
14	Butenal	13.88	72	123-72-8	0.03	Trace
15	Methyl vinyl ketone	14.24	70	78-94-4	0.16	Trace
16	2,3-Butanedione (diacetyl)	14.50	86	431-03-8	0.21	Trace
17	Benzene	16.44	78	71-43-2	0.02	Trace
18	Hydroxyacetaldehyde (glycol aldehyde)	17.76	60	141-46-8	<b>4.89</b>	0.99
19	2,5-Dimethylfuran	18.58	96	625-86-5	0.23	0.35
20	Formic acid	18.64	46	64-18-6	0.02	Trace
21	2-Butenal (Z)	19.43	70	15798-64-8	0.15	Trace
22	2-Methyl-2-propenal	19.52	70	78-85-3	0.21	Trace
23	Ethanol	19.86	46	64-17-5	0.01	Trace
24	Acetic acid	20.11	60	64-19-7	0.37	1.08
25	Vinylfuran	20.87	94	1487-18-9	0.16	Trace
26	2,3-Pentandione	21.20	100	600-14-6	0.01	Trace
27	Ethyl-1-propenyl ether	22.33	86	928-55-2	0.21	Trace
28	1-Hydroxy-2-propanone (acetol)	22.48	74	116-09-6	0.71	0.52
29	Toluene	23.07	92	108-88-3	0.12	Trace
30	2-Ethyl-5-methylfuran+methyl formate?	23.80	110	1703-52-2	0.14	Trace
31	Hydroxyacetic acid (glycolic acid)	24.63	76	79-14-1	0.01	Trace
32	2-Hydroxypropanoic acid (lactic acid)	24.96	90	50-21-5	Trace	Trace
33	2,3-Dihydro-1,4-dioxin	25.11	86	543-75-9	0.03	Trace
34	3-Methylfuran	25.70	82	930-27-8	0.22	Trace
35	2-Propenoic acid methyl ester?	26.69	86	96-33-3	0.44	0.41
36	1-Hydroxy-2-butanone	27.61	88	5077-67-8	0.08	Trace
37	1,4-Dioxadiene	28.91	84	N/A	<b>5.79</b>	<b>0.78</b>
38	3-Furaldehyde	29.12	96	498-60-2	0.24	Trace
39	2-Oxopropionic acid methyl ester?	29.33	102	600-22-6	0.13	0.12
40	Butandial	29.65	86	638-37-9	0.25	0.14

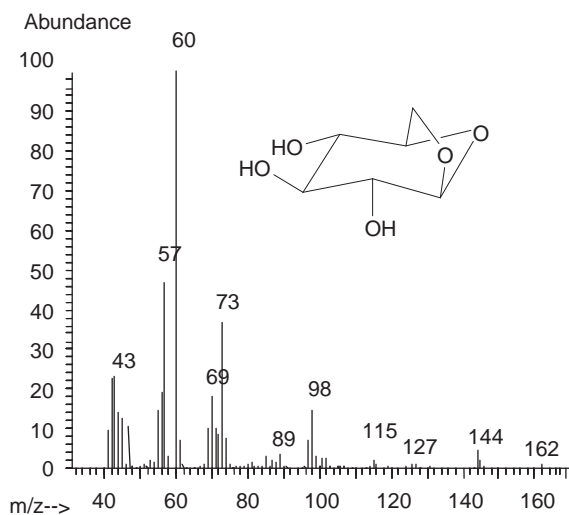
TABLE 16.1.2. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Glucose moles percent	Fructose moles percent
41	2-Cyclopentene-1,4-dione	30.27	96	930-60-9	0.23	Trace
42	Furancarboxaldehyde (furfural)	30.39	96	98-01-1	<b>11.49</b>	<b>26.74</b>
43	2-Propylfuran	30.83	110	4229-91-8	0.85	Trace
44	2-Furanmethanol	31.70	98	98-00-0	0.12	0.10
45	5-Methyl-2(3H)-furanone	32.05	98	591-12-8	0.18	Trace
46	Methylglyoxal+unknown	32.65	72	78-98-8	0.13	Trace
47	1-(2-furanyl)ethanone	33.15	110	1192-62-7	0.31	0.31
48	5-Methylidenfuran-2-one (protoanemonin)	33.93	96	108-28-1	0.11	Trace
49	2,4-Dihydroxy-2,5-dimethyl-2(2H)-furan-3-one	33.95	144	10230-62-3	Trace	Trace
50	Dihydro-4-hydroxy-2(3H)-furanone	34.13	102	5469-16-9	3.07	0.22
51	Dihydro-3-methylene-2(3H)-furanone	34.40	98	547-65-9	0.12	0.13
52	2-Hydroxy-2-cyclopenten-1-one	34.53	98	10493-98-8	0.48	0.39
53	Unknown	34.65	112	N/A	0.12	0.14
54	Isomaltol	34.92	126	3420-59-5	0.12	Trace
55	Benzaldehyde+unknown	34.99	106	100-52-7	0.14	0.17
56	2-Methylenecyclopentanol	35.39	98	20461-31-8	0.25	Trace
57	5-Methyl-2-furancarboxaldehyde	35.60	110	620-02-0	1.04	1.38
58	3-Methyl-2-cyclopenten-1-one	36.35	96	2758-18-1	0.13	Trace
59	7,8-Dioxabicyclo[3.2.1]oct-2-ene (mix)	36.53	112	N/A	0.16	Trace
60	Tetrahydro-4H-pyran-4-one	36.75	100	29943-42-8	0.46	Trace
61	Dihydro-5-propyl-2(3H)furanone?	36.96	128	105-21-5	0.14	0.16
62	6,8-Dioxabicyclo[3.2.1]octane	37.43	114	280-16-0	0.51	0.32
63	1,3-dihydroxy-2-propanone	37.74	90	96-26-4	1.41	2.66
64	2-Hydroxy-3-methyl-2-cyclopenten-1-one (cyclozene)	37.97	112	80-71-7	0.53	0.24
65	Isomer of 2-hydroxy-3-methyl-2-cyclopenten-1-one	38.21	112	N/A	0.32	Trace
66	Phenol	38.67	94	108-95-2	0.19	0.11
67	1,5-Hexadien-3-ol	38.85	98	924-41-4	0.29	Trace
68	4,5-Dimethyl-1,3-dioxol-2-one?	39.36	114	37830-90-3	0.25	0.39
69	2,5-Dimethyl-4-hydroxy-2-Hydrofuran-3-one?	39.72	128	3658-77-3	0.09	Trace
70	Unknown	39.89	144	N/A	0.29	0.60
71	2-Methylphenol (o-cresol)	40.25	108	95-48-7	0.09	Trace
72	Unknown	40.41	82	N/A	0.08	Trace
73	3-Furancarboxylic acid methyl ester	40.87	126	13129-23-2	0.87	0.84
74	3-Hydroxy-2-methyl-4H-pyran-4-one (maltol)	41.18	126	118-71-8	0.41	Trace
75	2,5-Furandicarboxaldehyde	41.42	124	823-82-5	0.49	0.61
76	Unknown	41.61	144	N/A	0.24	0.31
77	4-Methylene-1,2-dioxolan-3-one?	41.94	114	N/A	0.41	Trace

TABLE 16.1.2. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Glucose moles percent	Fructose moles percent
78	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	42.66	144	28564-83-2	0.46	1.34
79	Levogluconone	42.99	126	37112-31-5	2.19	0.10
80	3,5-Dihydroxy-2-methyl-4H-pyran-4-one (hydroxymaltol)	43.17	142	1073-96-7	0.23	0.15
81	2-Methyl-2-pentenoic acid	43.75	114	16957-70-3	0.16	Trace
82	Dianhydro sugar	44.89	144	N/A	0.06	Trace
83	Unknown	45.47	98	N/A	0.39	0.98
84	5-Acetoxymethyl-2-furaldehyde	45.68	168	10551-58-3	0.74	0.46
85	1,4:3,6-Dianhydro- $\alpha$ -D-glucopyranose	46.37	144	N/A	2.67	Trace
86	Unknown	46.96	116	N/A	Trace	0.21
87	5-Acetoxymethyl-2-furancarboxaldehyde	47.35	126	10551-58-3	Trace	0.26
88	5-(hydroxymethyl)-2-furancarboxaldehyde	47.68	126	67-47-0	<b>10.33</b>	<b>30.13</b>
89	3-Methyl-1,2-cyclopentanediol	48.26	116	27583-37-5	0.39	Trace
90	2',3'-Dideoxyribonolactone?	48.43	116	32780-06-6	Trace	0.25
91	1,2-Cyclohexanediol?	49.38	116	1792-81-0	1.07	0.44
92	Dianhydro sugar?	49.91	144	N/A	1.30	Trace
93	Unknown	56.04	198	N/A	Trace	0.45
94	Unknown	56.30	198	N/A	Trace	0.42
95	1,6-Anhydro- $\beta$ -D-glucopyranose (levoglucosan)	56.72	162	498-07-7	<b>11.00</b>	0.32
96	1,6-Anhydro- $\beta$ -D-glucofuranose	59.90	162	7425-74-3	<b>3.03</b>	0.12

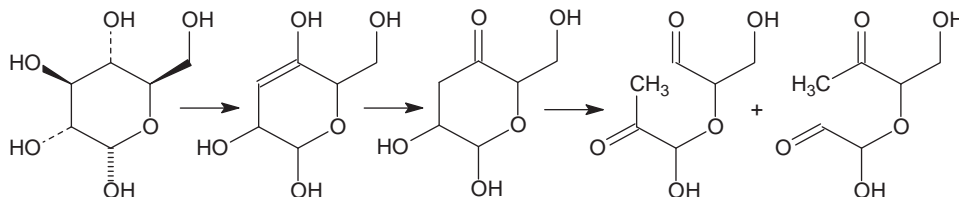
Notes: Numbers in bold indicate the major pyrolysis constituents.  
Hydrogen, CO, methane, ethane, and water not included.

FIGURE 16.1.6. Mass spectrum of 1,6-anhydro- $\beta$ -D-glucopyranose (levoglucosan).

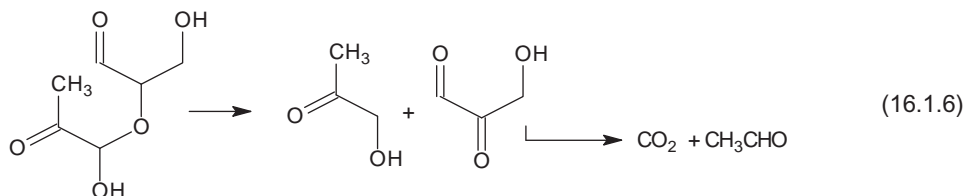




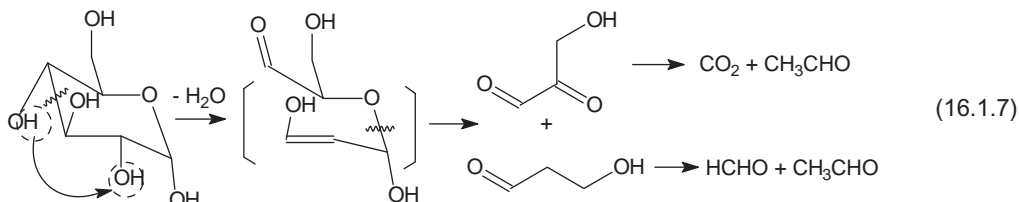
shown below for the pair C<sub>3</sub> and C<sub>4</sub> and the elimination of the OH from C<sub>3</sub> of glucose molecule:



The resulting compounds continue the decomposition process as shown below for one of the resulting aldehydes:

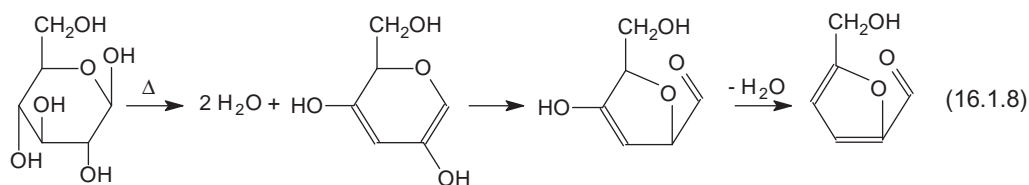


The elimination of water can occur also following a Grob fragmentation (see Section 2.3) that takes place for a 1,3-alcohol [17]. Since glucose has several pairs of 1,3-carbons with OH substituents, the reaction may generate a multitude of reaction products (as was mentioned for the water elimination between OH groups at vicinal atoms). For the structural formula of glucose the reaction is exemplified below between the OH groups at C<sub>2</sub> and C<sub>4</sub> atoms and cleavage of C<sub>3</sub>–C<sub>4</sub> bond in the molecule:

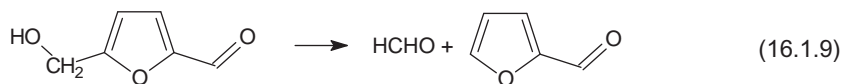


The initially formed fragments can further pyrolyze to generate CO<sub>2</sub> and small aldehydes, ketones, hydroxyaldehydes, etc. The water elimination from OH groups bound to 1,3-carbons is influenced by their position as *syn* or *anti* (*syn* favored), but water can be eliminated from both types. The formation of formaldehyde by reaction 16.1.7 does not account for the whole amount of this compound formed from glucose. As shown in Table 16.1.2, formaldehyde represents about 9% (moles) of pyrolysate, and its generation is likely to occur from other reactions. Addition of diammonium phosphate during glucose pyrolysis was shown to diminish the formation of formaldehyde [18]. It is likely that diammonium phosphate (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> has a catalytic effect on the opening of the internal hemiacetal structure [19], which leads to somewhat different reactions during glucose pyrolysis and also generates ammonia that reacts with HCHO diminishing its apparent level.

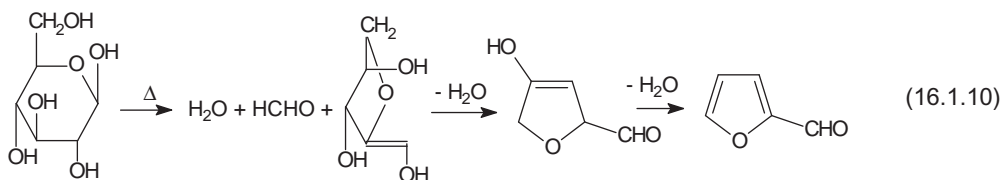
Water elimination also can have as a result the formation of various cycles. The formation of a furan derivative, 5-(hydroxymethyl)-2-furancarboxaldehyde (hydroxymethylfurfural) is shown, as an example, in the following sequence of reactions:



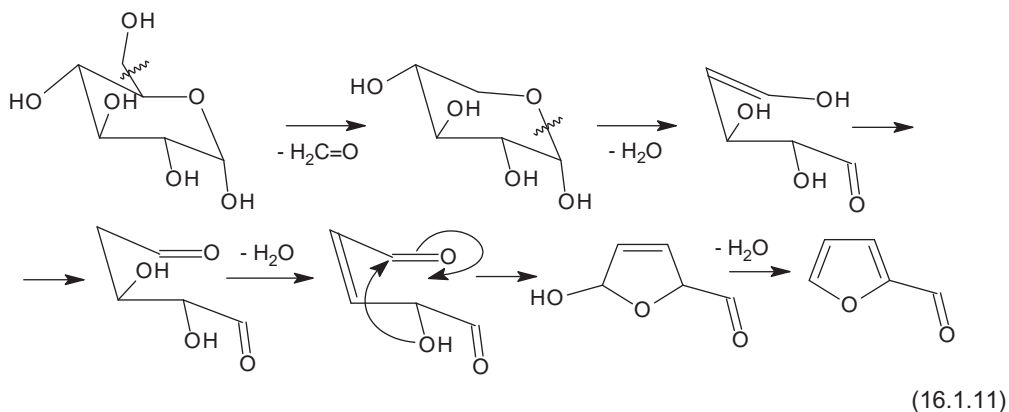
Hydroxymethylfurfural may further decompose to generate furancarboxaldehyde (furfural) and formaldehyde as shown in reaction 16.1.9:



Other reactions may also be responsible for the formation of furfural, one example being shown below:

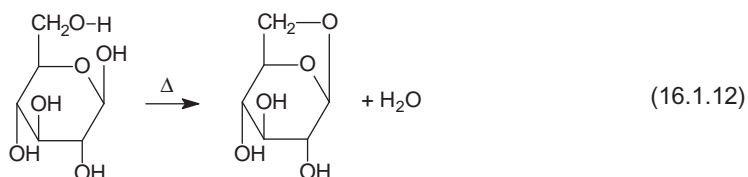


Another path also starts with formaldehyde elimination, but the cyclization process is assumed to occur in a later stage, as shown in the following sequence of reactions [20]:



The formation of furfural also can be explained starting with the linear form of glucose [20], although the low level of this form in solid glucose makes this mechanism unlikely.

The formation of pyran derivatives can result from various reactions affecting the OH and CH<sub>2</sub>OH groups, without affecting the initial pyran cycle of glucose. However, the formation of new six-atom rings containing one oxygen is also possible. An example of reaction with the preservation of the pyran cycle from glucose (and with formation of a new 1,3-dioxolane cycle) is the formation of levoglucosan by the elimination of one water molecule between the OH in 1-position of glucose and the H from the OH group connected to 6-position:



Further decomposition of levoglucosan generates pyrolysis products similar to those from glucose [21,22]. Figure 16.1.8 shows the comparison between the pyrogram of 1 mg glucose (the same shown in Figure 16.1.5) and the pyrogram of 1 mg levoglucosan (1,6-anhydro glucose) with the pyrolysis

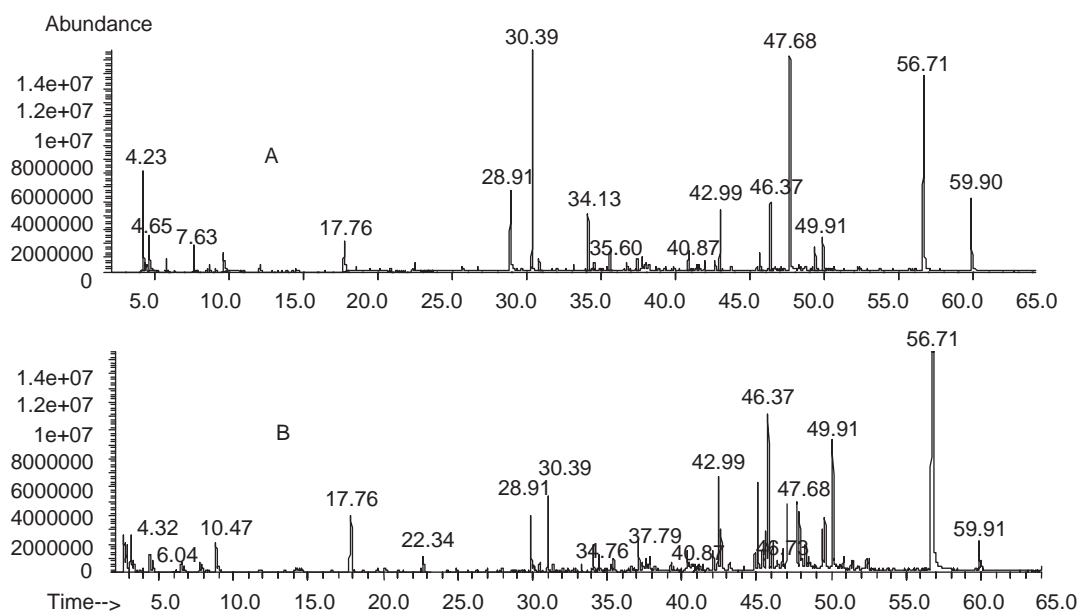
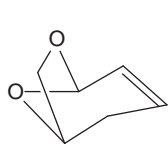


FIGURE 16.1.8. Pyrogram of 1 mg glucose (Trace A) and of 1.0 mg levoglucosan (Trace B) at 900 °C.

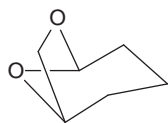
performed in identical conditions with that of glucose pyrolyzed at 900 °C. Glucose pyrolysate is shown in Trace A and levoglucosan pyrolysate in Trace B.

Detailed inspection of the two pyrograms from Figure 16.1.8 (using the data analysis capability of a GC/MS system) shows qualitative identity of most compounds, although some differences are seen in peak intensities. This indicates that pyrolysis of levoglucosan, initially formed during glucose pyrolysis, is a likely contributor to the formation of other molecules in glucose pyrolysate. However, this does not indicate that other reactions do not occur independently during pyrolysis of glucose, starting directly from the parent molecule. The lack of levoglucosan formation in fructose pyrolysis (see further), and the similarity in the nature of compounds generated from glucose and fructose is additional proof that levoglucosan formation is not the unique path of glucose pyrolysis.

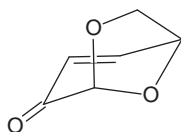
Besides levoglucosan, several other anhydro sugars are generated during glucose pyrolysis. The formulas for several of these compounds (including levoglucosan) detected in glucose pyrolysate are shown below:



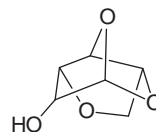
7,8-dioxabicyclo[3,2,1]oct-2-ene MW = 112



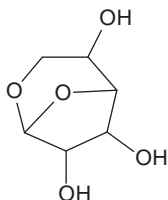
6,8-dioxabicyclo[3,2,1]octane MW = 114



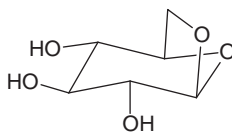
1,6-anhydro-3,4-dideoxy- $\beta$ -D-pyranose-2-one (levoglucosenone) MW = 126



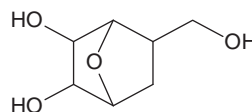
1,4:3,6-anhydro- $\alpha$ -D-glucopyranose MW = 144



1,6-anhydro- $\beta$ -D-glucofuranose MW = 162

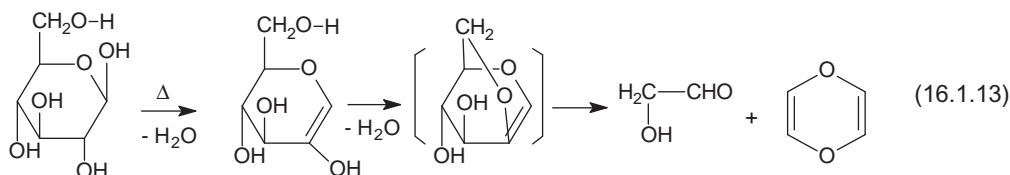


1,6-anhydro- $\beta$ -D-glucopyranose (levoglucosan) MW = 162



1,4-anhydro- $\beta$ -D-glucopyranose MW = 162

Besides the furan and pyran cycles, the anhydro sugars contain other oxygenated cycles. A reaction leading to the formation of a dioxane derivative (1,4-dioxadiene) is shown below:



The formation of a double bond at the bridgehead not being allowed (Bredt's rule, see Chapter 2), the elimination of the second water molecule leads to the fragmentation that gives dioxandiene and hydroxyacetaldehyde. Dioxane derivatives also can be formed from other reactions during glucose pyrolysis.

Glucose pyrolysate contains a number of compounds with multiple OH groups, and some of these compounds may not elute from the chromatographic column when conditions given in Table 4.6.1 are used. For this reason, a second experiment was performed by pyrolyzing 1.0 mg glucose at 900 °C followed by the collection of the pyrolysate and derivatization with BSTFA under conditions described in Section 4.6. The analysis of the derivatized pyrolysate was done with GC/MS technique under conditions described in Table 4.6.2. The chromatogram of the derivatized pyrolysate is shown in Figure 16.1.9.

The peak identification in the chromatogram from Figure 16.1.9 was done using mass spectra library searches. Only some of the peaks were identified and are listed in Table 16.1.3 as a function of their retention time.

The results shown in Table 16.1.3 indicate that besides the compounds already identified in Table 16.1.1, three new groups of compounds are present in the pyrolysate. The first group consists of several sugar fragment molecules including traces of ethylene glycol and ethylene glycol ethers, traces of a few sugar related acids, which include glyceric acid and ribonic acid (?), a gluconic acid lactone, and two isomers of trihydroxybenzene. No gluconic acid or deoxygluconic acid were detected in the pyrolysate. The presence of trihydroxybenzenes indicates the possibility of the formation of aromatic compounds in sugars pyrolysis. The second group consists of several monosaccharides. The compounds from this group were present at levels between 0.5% and 6% (molar) from that of levoglucosan (taken as 100%). Glucose is present in this group at about 0.8% level compared to levoglucosan. The third group consists of several disaccharides (including maltose). The presence of disaccharides shows that under the influence of heat, two molecules of glucose can eliminate water to form disaccharides. The compounds from this group were present at levels around 0.3% (molar) from that of levoglucosan and represented

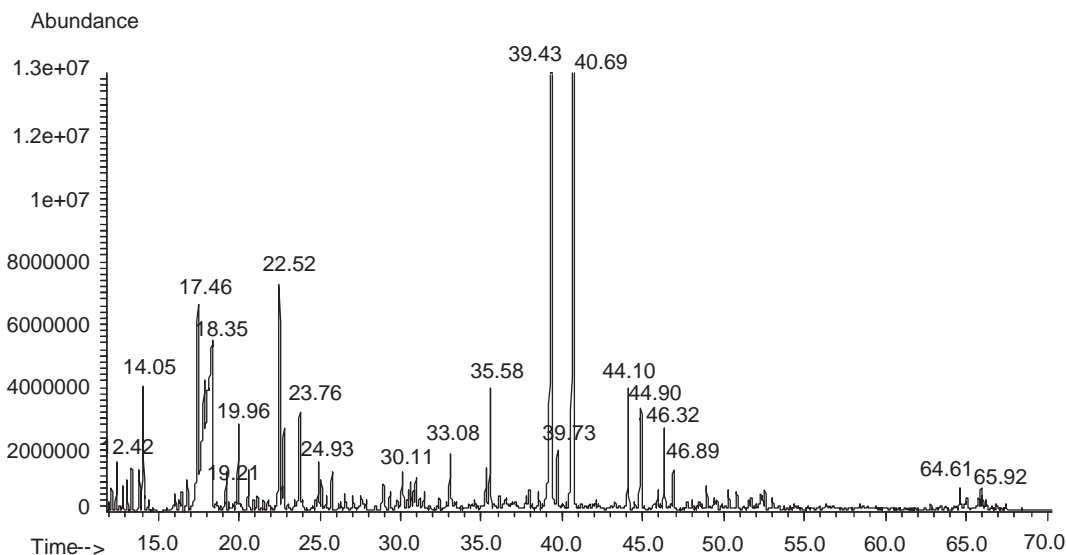


FIGURE 16.1.9. Chromatogram of the silylated pyrolysate of 1 mg D-(+)-glucose. Pyrolysis performed at 900 °C and derivatization done with BSTFA.

TABLE 16.1.3. Identification of the main peaks in the chromatogram shown in Figure 16.1.9 for the pyrolysate of glucose derivatized with bis(trimethylsilyl)trifluoroacetamide (BSTFA) and their molar levels relative to levoglucosan

No.	Compound	Ret. time	MW	Fragment ions m/z (intensity)	Percent to levoglucosan
1	Lactic acid 2 TMS	12.65	262	73(100), 147(50), 131(38), 205(11), 247(7)	3.09
2	Ethylene glycol 2 TMS	13.09	206	73(100), 147(85), 191(78)	2.49
3	Glycolic acid 2 TMS	13.53	220	73(100), 147(78), 66 (20), 205(17), 177(11)	3.80
4	2-Hydroxy-cyclopenten-1-one TMS	16.07	170	155(100), 81(25), 75(17), 73(17)	1.89
5	Hydrolyzed reagent	18.35	?	99(100), 44(30), 69(25)	—
6	Dihydroxyacetone 2 TMS	19.97	234	73(100), 103(44), 189(10), 219(4)	6.56
7	1,4-dioxan-2,5-diol 2 TMS	22.52	264	117(100), 161(79), 73(76), 191(8), 263(1)	18.58
8	2-(2-Hydroxyethoxy)ethan-1-ol 2 TMS	22.79	250	117(100), 161(85), 73(85), 191(12), 245(3)	5.77
9	5-(hydroxymethyl)furan-carboxaldehyde TMS	23.76	198	183(100), 109(34), 111(28), 169(14), 198(4)	9.76
10	Glyceric acid 3 TMS	24.63	322	73(100), 147(72), 189(50), 292(38)	4.21
11	2-Furanhydroxyacetic acid 2 TMS	26.56	286	169(100), 73(58), 147(30), 243(13), 286(3)	1.83
12	1,4:3,6-Anhydro- $\alpha$ -D-glucopyranose TMS	27.57	216	73(100), 75(50), 201(45), 191(15)	1.54
13	2-[2-(2-hydroxyethoxy)ethoxy]ethan-1-ol 2 TMS	30.12	308	117(100), 73(55), 103 (20) 161(20)	3.96
14	1,2,3-Trihydroxybenzene 3 TMS	32.96	342	239(100), 73(100), 342(54), 327(10)	0.05
15	Unknown	33.08	?	73(100), 258(55), 103(35), 185(30)	—
16	Trihydroxybenzene 3 TMS	35.52		239(100), 73(100), 342(54), 327(10)	0.05
17	I.S. tert-butylhydroquinone 2 TMS	35.58	310	310(100), 295(99), 73(53)	8.32
18	Ribonic acid 5 TMS?	37.11	526	73(100), 292(30), 147(25), 103(24), 421(1)	0.91
19	1,6-Anhydroglucofuranose 3 TMS	37.97	378	73(100), 147(55), 217(43), 205(30)	1.89
20	Anhydro sugar 3 TMS	38.55	378	73(100), 217(70), 204(66), 333(20)	1.16
21	Levoglucosan 3 TMS	39.43	378	73(100), 204(48), 217(42), 147(18), 333(19)	100.00
22	Anhydro sugar 3 TMS	39.73	378	73(100), 217(88), 191(64), 204(21), 430(10)	2.71
23	1,4-Anhydroglucopyranose 3 TMS	40.70	378	217(100), 73(20), 319(10)	43.56
24	Hexose 5 TMS	44.10	540	217(100), 73 (62), 204(56), 103(37), 363(1)	4.20
25	Hexose 5 TMS	44.90	540	73(100), 204(76), 103(52), 217(40), 259(13), 363(1)	6.17
26	Glucose 5 TMS	45.93	540	204(100), 191(40), 73(37), 217(19), 147(20), 435(2)	0.75

TABLE 16.1.3. *cont'd*

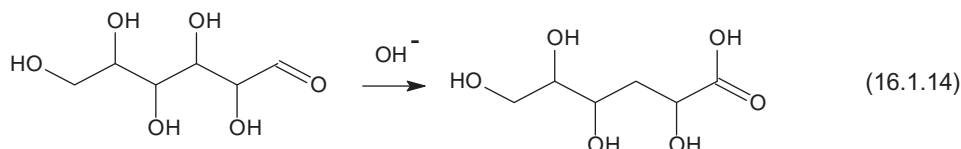
No.	Compound	Ret. time	MW	Fragment ions m/z (intensity)	Percent to levoglucosan
27	Gluconic acid lactone 4 TMS	46.09	466	73(100), 217(46), 147(38), 333(12), 466(10)	0.05
28	$\beta$ -D-Galactofuranose 5 TMS?	46.33	540	217(100), 73(80), 103(33), 247(14), 319(2)	3.03
29	Hexose 5 TMS	46.89	540	217(100), 73(49), 103(18), 243(11)	1.69
30	Gluconic acid 6 TMS	48.60	628	73(100), 333(25), 292(23), 147(20), 423(4)	0.15
31	Glucose 5 TMS	48.96	540	204(100), 191(47), 73(49), 217(19), 147(19), 435(2)	0.81
32	Hexose 5 TMS	50.30	540	73(100), 217(70), 204(53), 103(34), 243(32), 407(8)	0.82
33	Hexose 5 TMS	50.82	540	73(100), 217(78), 243(43), 205(40), 204(37), 407(14)	0.50
34	Hexose 5 TMS	52.55	540	73(100), 217(63), 205(53), 204(49), 147(35), 243(16)	0.70
35	Disaccharide 8 TMS	64.61	918	204(100), 217(57), 73(55), 361(29), 147(18), 451(1)	0.51
36	Disaccharide 8 TMS	64.95	918	204(100), 73(93), 217(80), 361(43), 271(31), 407(7)	0.38
37	Disaccharide 8 TMS	65.09	918	217(100), 73(98), 271(44), 204(31), 205(24), 489(2)	0.23
38	Disaccharide 8 TMS	65.77	918	73(100), 361(84), 217(80), 308(20), 319(10), 407(4)	0.38
39	Disaccharide 8 TMS	65.92	918	73(100), 217(60), 205(52), 246(42), 233(32), 473(2)	0.42
40	Disaccharide 8 TMS	66.02	918	204(100), 73(93), 361(74), 217(69), 147(24), 451(1)	0.30
41	Disaccharide 8 TMS	66.25	918	73(100), 217(74), 205(55), 233(44), 189(23), 473(3)	0.15

about 2% from the total area in the chromatogram. Similar results regarding silylated pyrolysate using hexamethyldisilazane [23] and online silylation [24] were reported in the literature.

One more group of compounds that was not listed in Table 16.1.2 and also not identified by the extension of the analyzed products by silylation and GC/MS analysis (Table 16.1.3) is the group of condensation products that have a high molecular weight. A considerable amount of char is generated by glucose pyrolysis, and besides carbon, the char contains a tar-type material. This tar is made from molecules resulting from the condensation of glucose molecules by elimination of water or by reactions between various fragments formed in the initial stages of pyrolysis. Also, this tar contains traces of other nonvolatile compounds such as PAHs. In an experiment designed to determine the levels of PAHs in glucose pyrolysis, a glucose sample was charred at 300 °C for 60 min and then heated at 600 °C for 10 min [25]. The analysis of the resulting levels of PAHs is shown in Figure 16.1.10.

The formation of PAHs in glucose pyrolysates is similar to the formation of PAHs in cellulose pyrolysate [26].

A considerable effort has been made in the study of thermo chemolysis of carbohydrates in the presence of TMAH [5]. In strong basic conditions and elevated temperature, carbohydrates have the tendency to form deoxyaldonic acids (saccharinic acids) in a reaction as shown below for a hexose (see reaction 2.5.2):



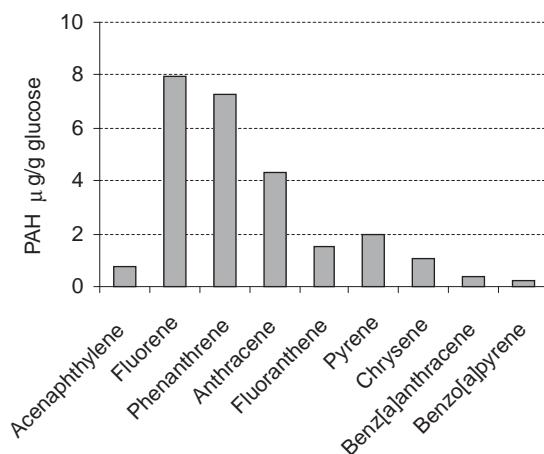


FIGURE 16.1.10. The level of PAHs in glucose pyrolysate at 300°C and then at 600°C [25].

TABLE 16.1.4. Main compounds identified in glucose pyrolysate at 700°C in the presence of TMAH [5]

No.	Compound	MW	Fragment ions (m/z)	Relative peak height
1	2-Methoxypropanoic acid methyl ester	118	59, 60, 75, 103, 118	65
2	2,4-Dimethoxy butanoic acid methyl ester	162	45, 72, 73, 75, 132	14
3	2,4,5-Trimethoxy-3-deoxy-D-threo-pentonic acid methyl ester	206	75, 101, 115, 129, 206	5
4	2,4,5-Trimethoxy-3-deoxy-D-erithro-pentonic acid methyl ester	206	75, 101, 115, 129, 206	9
5	Trimethoxybenzene	168	93, 110, 125, 153, 168	15
6	2,4,5,6-Tetramethoxy-3-deoxy-D-arabino-hexonic acid methyl ester	234	75, 101, 129, 159, 191	70
7	4,5,6-Tetramethoxy-3-deoxy-D-ribo-hexonic acid methyl ester	264	75, 101, 129, 159, 191	100

The resulting acid is further methylated by TMAH. Molecular fragmentation is also produced by the elevated temperatures, and the result is the formation of numerous methylated compounds, the main ones formed from the thermo chemolysis/methylation of glucose are given in Table 16.1.4 [5].

Thermo chemolysis/methylation in the presence of TMAH has been applied on various carbohydrates with the goal of characterization of saccharides in biomaterials [5,27].

### Mannose and galactose

The pyrograms of two other hexoses, mannose and galactose, which are typically found mainly in pyranose form (mannose ~100% and galactose ~93%) are given in Figure 16.1.11 Trace A and B, respectively. The pyrolysis and the pyrograms were obtained in identical conditions as for glucose, at 900 °C.

The peaks eluting up to 50 min in the pyrograms shown in Figure 16.1.11 Trace A and B are identical in nature with those generated from glucose and can be identified by their retention times in

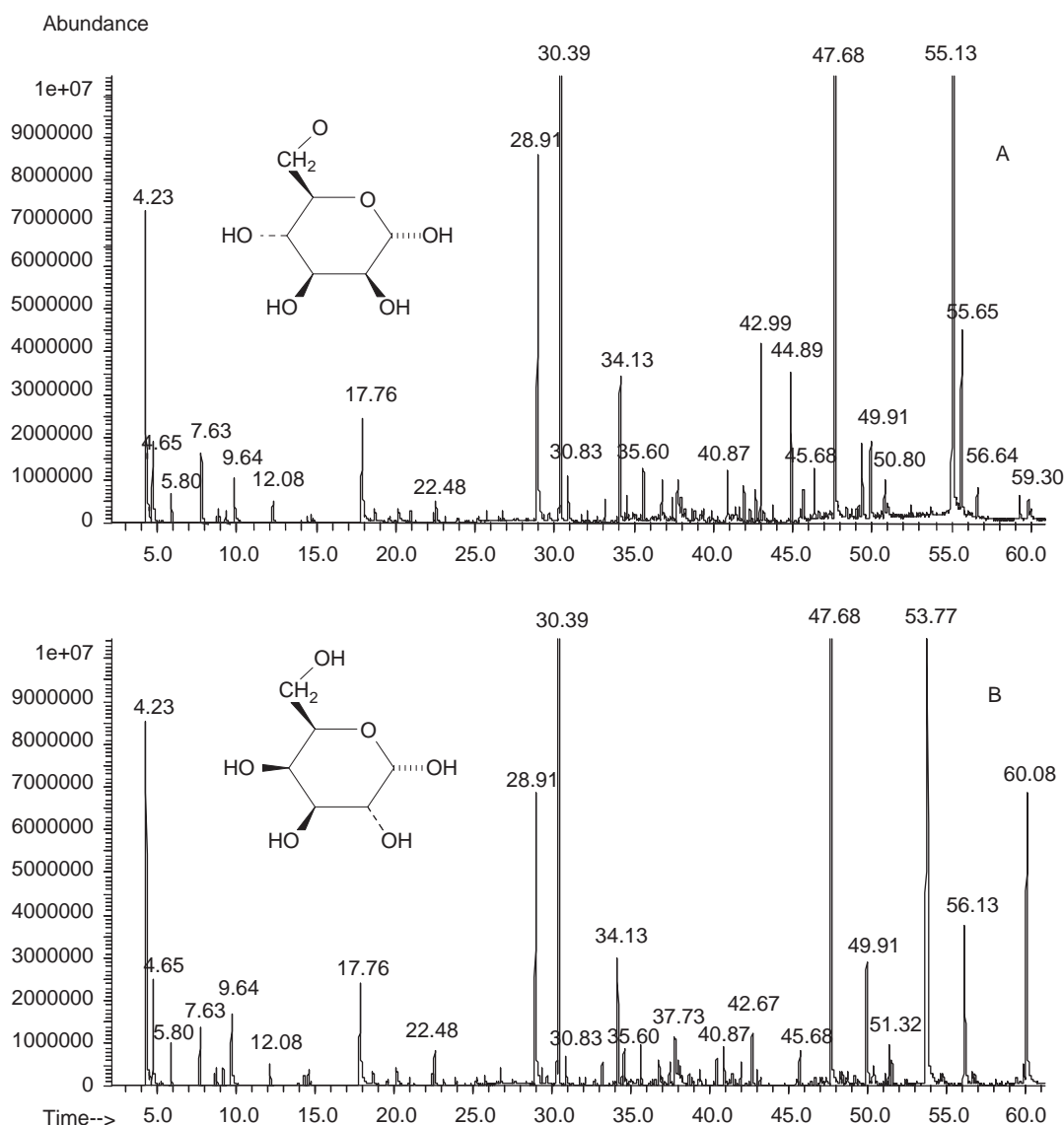


FIGURE 16.1.11. Pyrograms of 1 mg mannose (Trace A) and 1.0 mg galactose (Trace B) at 900 °C.

Table 16.1.2. The major peaks belong to CO<sub>2</sub>. Similar to the case of pentoses, toward the end of the pyrogram are eluting anhydro sugars that retain some of the chiral centers of the parent molecule. Anhydro sugar diastereoisomers were generated from glucose, mannose, and galactose, respectively. These compounds elute at different retention times as seen by comparing the pyrograms shown in Figures 16.1.5 for glucose, and 16.1.11A and 16.1.11B for mannose and galactose, respectively. The identification of the main peaks eluting at higher retention times than 50 min in the pyrograms of mannose and galactose is given in Table 16.1.5.

The GC/MS analysis of anhydro sugars formed by pyrolysis of monosaccharides and retaining OH groups bound to chiral carbons is better performed using off-line derivatization of these compounds after pyrolysis. A time window (37.0–46.0 min) from the chromatograms of trimethylsilyl (TMS) derivatives of the pyrolysates of (a) mannose, (b) allose, (c) galactose, and (d) glucose is shown in Figure 16.1.12, with the peak identification in Table 16.1.6. Pyrolysis of these hexoses was done at 590 °C [2].



TABLE 16.1.5. Identification of the peaks eluting at retention times higher than 50 min in the pyrograms of mannose and galactose shown in Figure 16.1.11 Trace A and B

No.	Compound	Ret. time (min)	MW	Mannose area (10 <sup>6</sup> )	Galactose area (10 <sup>6</sup> )
1	1,4-Anhydromannopyranose	50.80	162	34.2	—
2	1,6-Anhydro- $\beta$ -galactopyranose	53.78	162	—	1156.5
3	1,6-Anhydro- $\beta$ -mannopyranose	55.14	162	744.5	—
4	1,6-Anhydro- $\alpha$ -galactofuranose	56.13	162	—	210.8
5	1,6-Anhydro- $\alpha$ -mannofuranose	55.63	162	200.4	—
6	Anhydropyranose	56.64	162	27.0	—
7	1,6-Anhydro- $\beta$ -D-glucofuranose?	59.85	162	19.9	—
8	Anhydrofuranose?	60.08	162	8.8	—
9	1,6-Anhydro- $\beta$ -galactopyranose	60.08	162	—	402.2

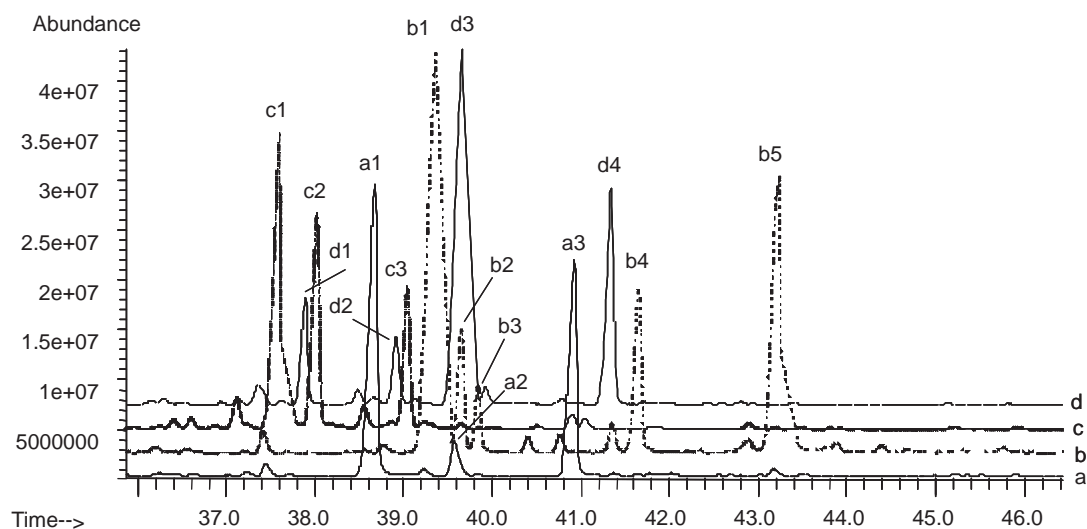


FIGURE 16.1.12. Time window between 40 min and 50 min from the chromatogram of TMS derivatives of pyrolysates of (a) mannose, (b) allose, (c) galactose, and (d) glucose showing anhydro sugars. Peak identification is given in Table 16.1.6 (at page 441).

As shown in Figure 16.1.12, the differences in the retention times for 1,6-anhydro sugars or 1,4-anhydro sugars from different parent molecules are noticeable. This is a proof that the anhydro sugars maintain part of the initial steric structure of the parent molecule.

### Fructose

Fructose is a hexose that is found mainly in furanose form. The pyrolysis products of fructose are similar in nature with those of other monosaccharides. An example of a pyrogram generated online at 900 °C from D-(–)-fructose is shown in Figure 16.1.13. The pyrolysis was done in conditions identical to those for glucose. The peak identification and relative molar content in 100 moles of pyrolysate are given in Table 16.1.2, together with those of glucose. The calculation of the mole percent was obtained based solely on peak areas.

TABLE 16.1.6. Identification of the peaks in the chromatogram shown in Figure 16.1.12 for the anhydro sugars formed during pyrolysis of four monosaccharides

Saccharide	Peak	Assignment
Mannose	a1	1,6- $\beta$ -Anhydromannopyranose
	a2	1,4-Anhydromannopyranose
	a3	1,6- $\alpha$ -Anhydromannofuranose
Allose	b1	1,6-Anhydroallopyranose
	b2	1,6-Anhydroglucopyranose (impurity in allose)
	b3	an Anhydrofuranose?
	b4	1,6-Anhydroallofuranose
	b5	1,4-Anhydroallopopyranose
Galactose	c1	1,6-Anhydrogalactopyranose
	c2	1,6-Anhydrogalactofuranose
	c3	1,4-Anhydrogalactopyranose
Glucose	d1	1,6-anhydroglucofuranose
	d2	1,4-Anhydroglucopyranose type?
	d3	1,6-Anhydroglucopyranose (levoglucosan)
	d4	1,4-Anhydroglucopyranose

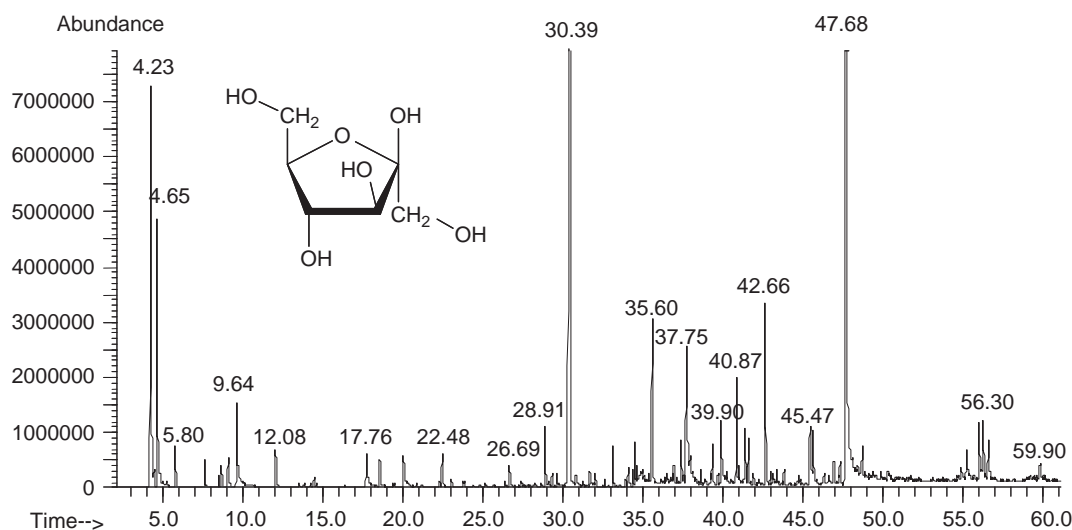


FIGURE 16.1.13. Pyrogram of 1.0 mg D-(-)-fructose at 900 °C. Peak assignment in Table 16.1.2.

Qualitatively, the composition of fructose pyrolysate is very similar to that of glucose. However, the proportion of various compounds in the two pyrograms is very different. Particularly, the dianhydro sugars seen in glucose pyrolysate are absent in that of fructose, and levoglucosan and 1,6-anhydro- $\beta$ -D-glucopyranose are present at significantly lower levels for fructose.

The experiment performed on fructose using pyrolysis at 900 °C followed by off-line derivatization with BSTFA and GC/MS analysis showed, except for the anhydro sugars, similar compounds as in the case of glucose, but with the levels very different. Another significant difference was noticed in the level of disaccharide generated from fructose in the specific conditions used for this experiment. The level of disaccharides was for fructose about 10 times higher than in the case of glucose (and represented about 16% from the total peak areas in the chromatogram). It was not possible to identify individual disaccharides in the mixture using mass spectral library searches.

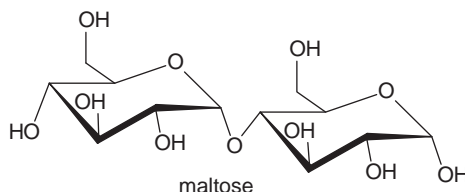
The mechanisms involved in fructose pyrolysis are similar to those proposed for explaining the composition of glucose pyrolysate. It is likely that other hexoses have similar pyrolysis products with the compounds discussed in this section, although the percentage of various components in the pyrolysate is likely to be different from compound to compound.

Differentiation between different monosaccharides for analytical purposes has been achieved successfully using the differences in the anhydro sugars generated by pyrolysis [7,12] or using thermally assisted hydrolysis and methylation (e.g., with TMAH as a reagent) followed by GC/MS analysis [5].

## 16.2. DISACCHARIDES

### General aspects

Disaccharides are formed by the elimination of a water molecule between two monosaccharides (different or identical) with the formation of an ether bond. Disaccharides have common names and systematic names and can be indicated by the names of the participating monosaccharides and the bond type. For example, maltose or 4-O- $\alpha$ -D-glucopyranosyl-D-glucose is indicated as Glc  $\alpha(1 \rightarrow 4)$  Glc. The elimination of water can take place between any of the OH groups of the participating monosaccharides, and more than one disaccharide can be formed even starting with identical monosaccharide molecules. For example, two glucose molecules connected  $\alpha(1 \rightarrow 4)$  form maltose and connected  $\alpha(1 \rightarrow 1)\alpha$  form trehalose. When a disaccharide is formed involving one OH group from the anomeric carbon, the same monosaccharide even connected to the OH at the same carbon on the other molecule can generate two different disaccharides. For example, two molecules of glucose connected  $\alpha(1 \rightarrow 4)$  form maltose, and two molecules of glucose connected  $\beta(1 \rightarrow 4)$  form cellobiose. When the water molecule is eliminated between anomeric carbons in both monosaccharides, the resulting disaccharide does not have reducing properties (monosaccharides and disaccharides having a free acetal OH group have reducing properties). The name of the nonreducing disaccharides replaces the end “ose” with “oside” suggesting the formation of a glycoside (see Section 16.3). The structure of disaccharides is amply described in the literature (see e.g., [28]).



### Maltose, lactose, and sucrose

Pyrolysis of disaccharides takes place following reactions very similar to those of monosaccharides. The nature of pyrolysis products from a disaccharide depends on the nature of the component monosaccharides and on the type of connection between the two monosaccharide molecules. For several  $1 \rightarrow 2$  or  $1 \rightarrow 4$  connected monosaccharides, the nature of the pyrolysis products is not very different from that of the pyrolysis of individual monosaccharides, but the proportion of various compounds in the pyrolysate may show differences. The decomposition starts around  $190^\circ\text{C}$  by losing  $\text{H}_2\text{O}$  and further decomposition takes place as the temperature increases. Flash pyrolysis at temperatures above  $650\text{--}700^\circ\text{C}$  up to about  $1000^\circ\text{C}$  generates various fragments of the molecules, similar to the case of monosaccharides. Pyrolysis of three disaccharides, maltose, lactose, and sucrose, was performed in identical conditions as for glucose, and the pyrograms are shown in Figure 16.2.1 for maltose (Trace A), for lactose (Trace B), and for sucrose (Trace C). Maltose is 4-O- $\alpha$ -D-glucopyranosyl-D-glucose (Glc  $\alpha(1 \rightarrow 4)$  Glc), lactose is  $\beta$ -D-galactopyranosyl-( $1 \leftrightarrow 4$ )- $\beta$ -D-glucopyranose (Gal  $\beta(1 \rightarrow 4)$  Glc), and sucrose is  $\alpha$ -D-glucopyranosyl-( $1 \leftrightarrow 2$ )- $\beta$ -D-fructofuranoside (Glc  $\alpha(1 \rightarrow 2)$  Fru).

Pyrolysis conditions were as described in Section 4.6 for Type 1 Experiment, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ . The analysis of pyrolysate was done

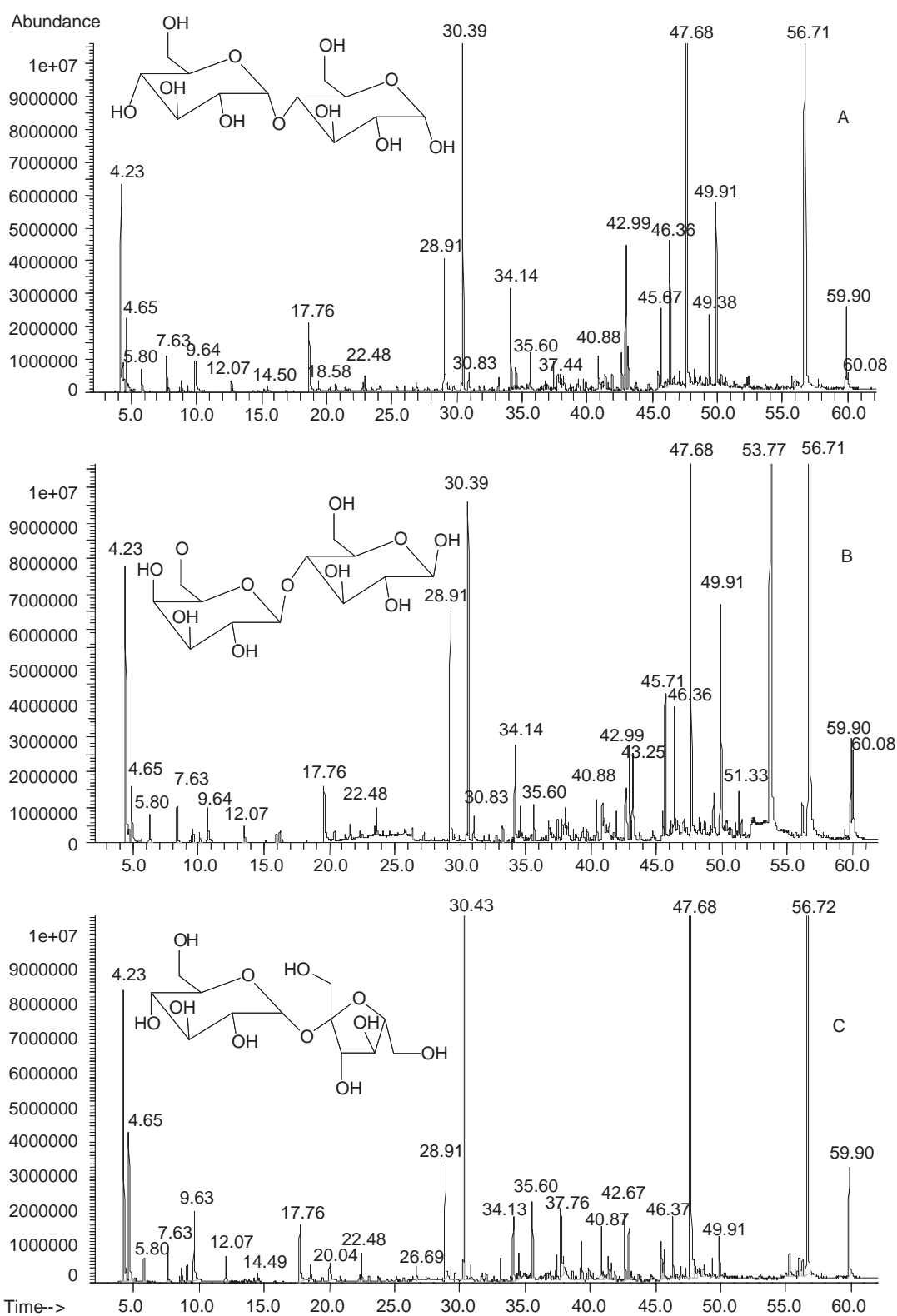


FIGURE 16.2.1. Pyrogram of 1.0 mg maltose Glc  $\alpha(1 \rightarrow 4)$  Glc (Trace A), 1.0 mg lactose Gal  $\beta(1 \rightarrow 4)$  Glc (Trace B), and 1.0 mg sucrose Glc  $\alpha(1 \rightarrow 2)$  Fru (Trace C) at 900°C.

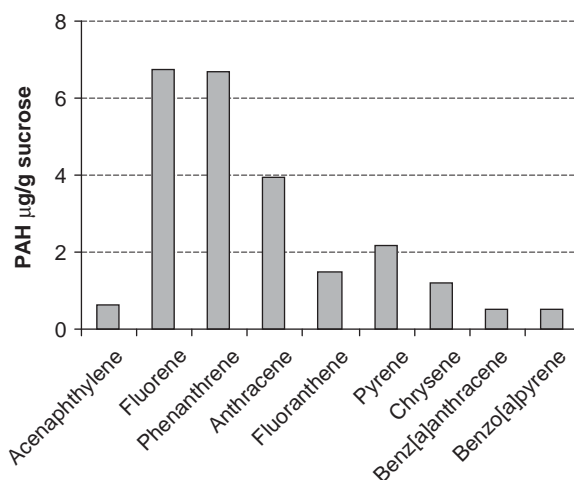


FIGURE 16.2.2. The level of PAHs in sucrose pyrolysate at 300°C and then at 600°C [25].

by GC/MS under conditions given in Table 4.6.1. Since the nature of the compounds in the three pyrolysates is the same as for glucose for all the compounds eluting before 50 min in the pyrogram, the compound identifications based on their retention time can be obtained from Table 16.1.2 (list for glucose). This window of the pyrogram is dominated by the peaks of CO<sub>2</sub> (2.23 min), 1,4-dioxadiene (28.91 min), furancarboxaldehyde (30.39 min), and 5-(hydroxymethyl)-2-furancarboxaldehyde (47.68 min). For the anhydro sugars that are formed from glucose, their identification is also given in Table 16.1.2, and for those generated from the galactose moiety, the identification can be done based on Table 16.1.5.

Pyrolysis of disaccharides typically starts with the cleavage of the ether bond between the two monosaccharide units [29]. This leads to the formation of a monosaccharide and a dehydrated derivative of the other monosaccharide. In the case of lactose, for example, the two molecules formed are 1,6-anhydro-β-D-galactopyranose (levoglucosan equivalent for galactose) and glucose. The resulting molecules continue to decompose under the influence of heat. Levoglucosan was shown to decompose very similarly to glucose (see Section 16.1), and the same properties can be assumed valid for other 1,6-anhydro sugars; therefore it is not possible to distinguish the origin of the resulting fragments as generated from a monosaccharide or from its 1,6-anhydro derivative. The formation of fragments by the cleavage of the ether bond between the monosaccharide units allows the formation of new di- or trisaccharides, typically identified at low levels in the pyrolysates of disaccharides. This formation of new condensation products between the disaccharide fragments was also verified in an experiment with sucrose thermal degradation, where the addition of erythritol ((2R,3S)-butane-1,2,3,4-tetraol) led to the formation of an erythritol fructoside [25]. Disaccharide pyrolysis also leads to the formation of a considerable amount of char, most of this material consisting of carbon but also containing various oligosaccharides.

The formation of PAHs from disaccharide pyrolysis has been found to be very similar to the formation of these compounds from monosaccharides or from cellulose [25]. The levels of several PAHs generated in sucrose charred at 300°C for 60 min and then heated at 600°C for 10 min is shown in Figure 16.2.2 [25].

### Rutinose

Rutinose or 6-O-α-L-rhamnosyl-D-glucose or 6-O-(6-deoxy-α-L-mannopyranosyl)-D-glucose is a disaccharide consisting of a rhamnose and a glucose molecule indicated as (Ram α(1→6) Glc). This compound is present in some glycosides such as rutin. Rutinose starts decomposing similarly to other disaccharides around 190°C. Pyrolysis of a sample of rutinose performed on 1.0 mg compound in a Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280^\circ\text{C}$ , generates the pyrogram shown in Figure 16.2.3. The analysis of

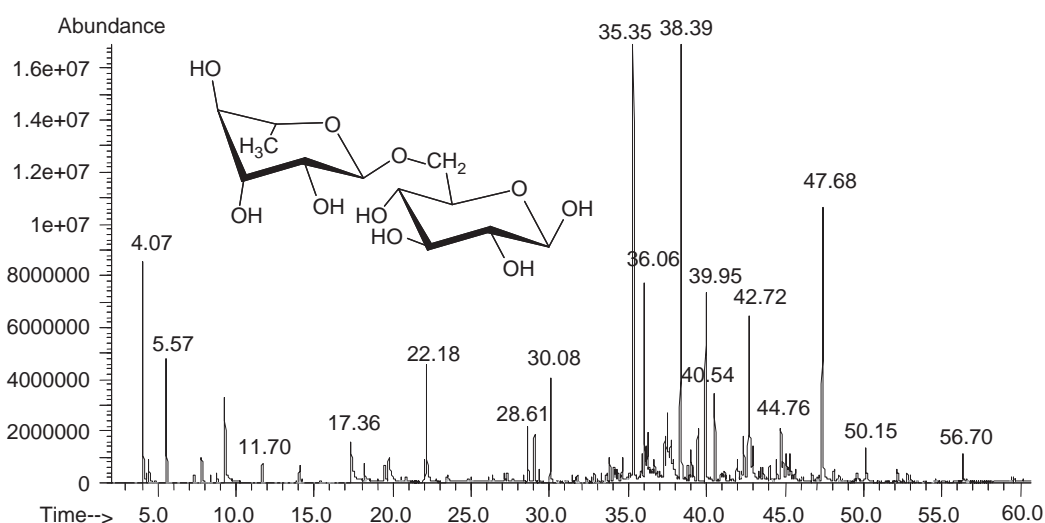


FIGURE 16.2.3. Pyrogram of 1.0 mg of rutinose Ram  $\alpha(1 \rightarrow 6)$  Glc at 900°C. Note: The retention times of the early peaks in the pyrogram from Figure 16.2.3 are shifted with about 0.3 min earlier compared to those from Figure 16.1.5 of glucose.

TABLE 16.2.1. Identification of the main peaks in the chromatogram shown in Figure 16.2.3 for the pyrolysis of rutinose

No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent
1	Carbon dioxide	4.07	44	124-38-9	<b>10.86</b>
2	Formaldehyde	4.49	30	50-00-0	1.96
3	Acetaldehyde	5.57	44	75-07-0	5.90
4	Ethanol	7.85	46	64-17-5	1.30
5	Pyruvaldehyde	9.32	72	78-98-8	3.70
6	Hydroxyacetaldehyde (glycol aldehyde)	17.36	60	141-46-8	3.81
7	Acetic acid	19.77	60	64-19-7	2.45
8	Ethyl-1-propenyl ether	22.03	86	928-55-2	0.71
9	1-Hydroxy-2-propanone (acetol)	22.18	74	116-09-6	5.07
10	1,4-Dioxadiene	28.61	84	N/A	1.90
11	2-Oxopropionic acid methyl ester?	29.04	102	600-22-6	0.95
12	Furancarboxaldehyde (furfural)	30.08	96	98-01-1	2.59
13	Furanyl ethanone	32.87	110	1192-62-7	0.10
14	Dihydro-4-hydroxy-2(3H)-furanone	33.86	102	5469-16-9	0.65
15	3-Hepten-2-one?	34.65	112	1119-44-4	0.59
16	5-Methyl-2-furancarboxaldehyde	35.34	110	620-02-0	<b>10.60</b>
17	3-Acetyldihydro-2(3H)-furanone	36.06	128	517-23-7	4.48
18	Tetrahydro-3,6-dimethyl-2H-pyran-2-one	36.25	128	3720-22-7	1.43
19	4-Penten-2-ol	37.35	86	625-31-0	2.03
20	1,3-Dihydroxy-2-propanone	37.52	90	96-26-4	3.60
21	2-Hydroxy-3-methyl-2-cyclopenten-1-one (cyclopentenone)	37.74	112	80-71-7	3.02
22	3-Hydroxy-5-methyl-5,6-dihydroxypyran-4-one	38.39	128	N/A	<b>10.38</b>

(Continued)

TABLE 16.2.1. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent
23	2,5-Dimethyl-4-hydroxy-3(2H)-furanone	39.45	128	3658-77-3	0.84
24	Unknown	39.95	128	N/A	3.67
25	Anhydro sugar from rhamnose?	40.54	144	N/A	1.42
26	Anhydro sugar from rhamnose?	42.36	144	N/A	1.37
27	Anhydro sugar from rhamnose?	42.72	144	35810-56-1	4.45
28	3,5-Dihydroxy-2-methyl-4H-pyran-4-one (hydroxymaltol)	42.95	142	1073-96-7	0.85
29	Dianhydromannitol	44.02	146	N/A	0.20
30	Unknown	44.77	128	N/A	1.78
31	5-(hydroxymethyl)-2-furancarboxaldehyde	47.68	126	67-47-0	6.05
32	Unknown	50.15	146	N/A	0.81
33	1,6-anhydro- $\beta$ -D-glucopyranose (levoglucosan)	56.70	162	498-07-7	0.47

Notes: Numbers in bold indicate the major pyrolysis constituents. Hydrogen, CO, methane, ethane, and water not included.

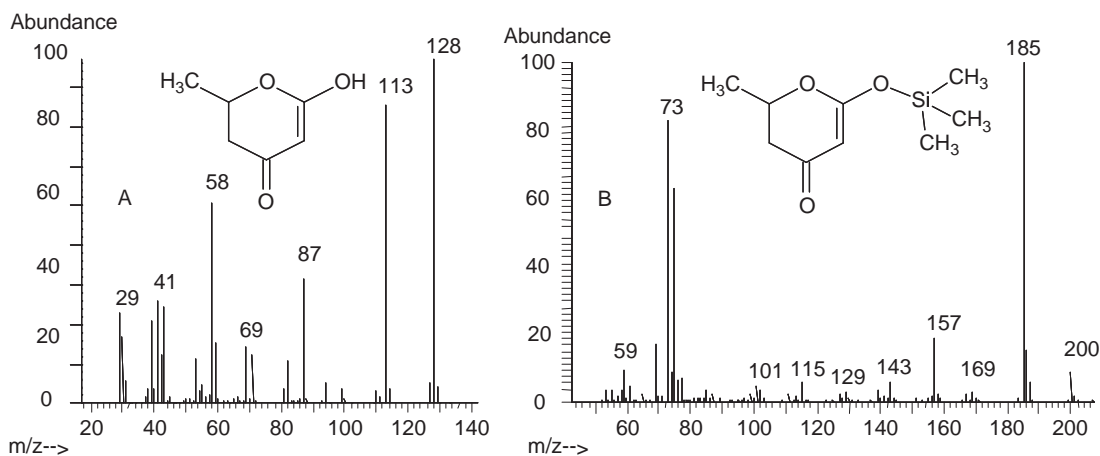


FIGURE 16.2.4. Mass spectrum of 3-hydroxy-5-methyl-5,6-dihydroxypyran-4-one (spectrum A) and its TMS derivative (spectrum B).

pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 16.2.1. The calculation of the mole percent was obtained based solely on peak areas.

The pyrogram of rutinose is rather different from that of other disaccharides. The main peaks in the pyrogram are CO<sub>2</sub>, 5-methyl-2-furancarboxaldehyde, and 3-hydroxy-5-methyl-5,6-dihydroxypyran-4-one. Since among the pyrolysis products of rutinose there are compounds that retain several OH groups from the parent compound, it can be expected that some pyrolysis products may not be seen in the pyrogram generated under conditions given in Table 4.6.1 since they do not elute from the chromatographic column. For the analysis of these compounds, the silylation of the pyrolysate followed by GC/MS analysis under conditions described in Table 4.6.2 is necessary. However, except for some undecomposed rutinose, no additional compounds were detected in the silylated pyrolysate. A confirmation of the formation of 3-hydroxy-5-methyl-5,6-dihydroxypyran-4-one was obtained following the analysis of the silylated pyrolysate, since this compound also generates a sizable peak in the chromatogram of the silylated pyrolysate. The mass spectra of 3-hydroxy-5-methyl-5,6-dihydroxypyran-4-one and its TMS derivative are shown in Figure 16.2.4A and 16.2.4B, respectively.

Important differences can be seen between the pyrolysis of other disaccharides and that of rutinose in the formation of anhydro sugars. The level of levoglucosan is very low in rutinose pyrolysate since the OH group from C<sub>6</sub> of glucose is involved in the ether link with the rhamnose unit, and it is not available to eliminate a water molecule between the OH groups at atoms 1 and 6. Also, instead of furfural formation, 5-methylfurfural is among the major pyrolysis products of rutinose. The pyrolysis of this compound shows that besides the component monosaccharides in a disaccharide, the type of bond between the monosaccharide units is also important for the pyrolysate composition.

### 16.3. CARBOHYDRATES WITH ADDITIONAL FUNCTIONAL GROUPS

A large variety of compounds are derived from carbohydrates. These compounds are generated by the modification of the initial carbohydrate molecule, either adding or subtracting functionalities. Several of the more common carbohydrate derivatives are indicated below.

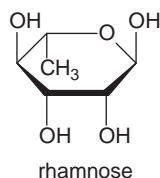
- The replacement of an OH group with hydrogen generates a special type of compound known as doxy sugars. Examples of these molecules are 2-deoxy-D-ribose((2R,4S,5R)-5-hydroxymethyltetrahydrofuran-2,4-diol), 6-deoxy-L-galactose (fucose), and 6-deoxy-L-mannose (rhamnose).
- Reduction (hydrogenation) of the aldehyde group(s) of a carbohydrate into alcohol generates a sugar alcohol. These compounds can be classified as polyols, and a discussion on their pyrolysis can be found in Section 9.1 (sorbitol or glucitol is discussed with some details). In the case of disaccharides (or trisaccharides, etc.) that are formed leaving free the OH at only one anomeric carbon, it is possible to change one sugar unit into a polyol, while the other(s) remains unaffected. For example, partial hydrogenation of maltose leads to 4-O- $\alpha$ -D-glucopyranosyl-D-glucitol (maltitol). These compounds are partly carbohydrate and partly polyol.
- Oxidation of a monosaccharide leads to the formation of sugar acids. There are numerous sugar acids that may have one or more carboxyl groups, and some may have additional modifications of the carbohydrate structure. Examples of sugars acids are gluconic acid, glucuronic acid, and ascorbic acid.
- Replacement of an OH group with chlorine (or other halogen) leads to halogenated sugars. Sucralose or 4,1',6'-trichloro-4,1',6'-trideoxygalactosucrose is a well-known halogenated sugar used as an artificial sweetener (sold under the trade name Splenda<sup>®</sup>).
- Ethers and silyl ethers are sugar derivatives obtained by the replacement of the active hydrogens from the OH groups with R or Si(R)<sub>3</sub> where R is an alkyl or aryl radical. These derivatives of sugars are frequently used in various syntheses and for analytical purposes. Formation for analytical purposes of TMS ethers after pyrolysis of sugars was previously described (see Section 16.1).
- Glycosides are a special class of ethers formed between the OH group from the anomeric carbon of a saccharide and a nonsugar molecule (this class does not include nonreducing disaccharides that involve the anomeric carbons in their formation). The nonsugar group of a glycoside is indicated as an aglycone. When the sugar moiety is glucose, the compounds are indicated as glucosides. Numerous glycosides are natural compounds.
- Sugar esters are compounds where one or more OH groups are esterified. The esterification can be done with a variety of acids, the most common esters being acetylated sugars.
- Simple amino sugars are compounds with an OH group replaced by an NH<sub>2</sub> group. The most common amino sugar is 2-amino-2-deoxy-D-glucose or (3R,4R,5S,6R)-3-amino-(hydroxymethyl)oxane-2,4,5-triol. The amino group can be acetylated to form N-acetylglucosamine, another common amino sugar. These molecules play a major role in biological systems, being involved in various glycosylation mechanisms. More complicated molecules also are known in this group of sugar derivatives. Among these are the derivatives that contain both amino and carboxyl groups (e.g., neuraminic acid).

#### Deoxy sugars

There is very little information in the literature regarding the pyrolysis of deoxy sugars. Pyrolysis of a rhamnose (6-deoxy-L-mannose) sample performed at 900 °C in conditions similar to that for glucose



showed that the compound behaves very similarly to other sugars during pyrolysis. Most small fragments generated from rhamnose are similar to those generated, for example, from glucose. Among the small fragments that were different in rhamnose pyrolysate compared to glucose were 1,2- and 1,3-propandiol and 2,5-dimethyl-4-hydroxy-3(2H)-furanone. The peak intensities were also relatively different. A number of compounds tentatively identified as anhydro-deoxy sugars resulting from the elimination of one or two water molecules from rhamnose were also present in the pyrolysate. However, only tentative assignments were possible since the mass spectra of these anhydro sugars were not available in common mass spectra libraries. Silylation of the rhamnose pyrolysate followed by GC/MS analysis showed that some rhamnose is still present in the pyrolysate, as well as several disaccharides resulting from the elimination of water between two rhamnose molecules. These disaccharides were present at levels around 0.5–1% in the pyrolysate.



### Compounds part carbohydrate part polyol

A typical example of a partially hydrogenated sugar is maltitol. This compound is formed from a glucose unit connected through the glucosidic OH with a glucitol (sorbitol) unit. The compound could be classified also as a glucoside. Pyrolysis of a sample of maltitol performed on 1.0 mg compound in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ , generates the pyrogram shown in Figure 16.3.1. The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 16.3.1. The calculation of the mole percent was obtained based solely on peak areas.

The results of the analysis of maltitol pyrolysate from Table 16.3.1 show a number of compounds that were identical in glucose (see Section 16.1) and sorbitol (see Section 9.1) pyrolysates, as well as

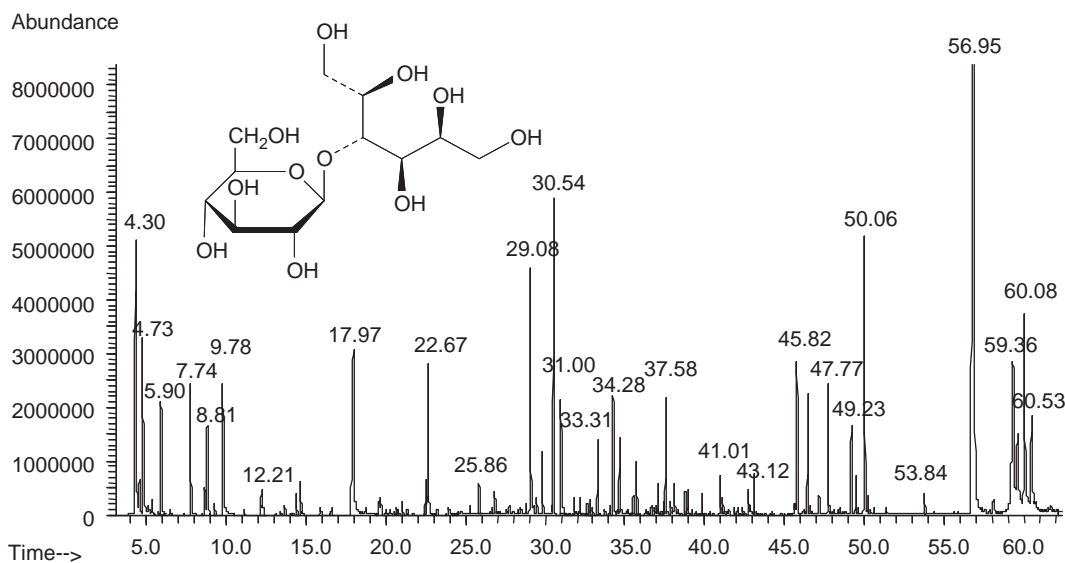


FIGURE 16.3.1. Pyrogram of 1 mg maltitol at  $900^\circ\text{C}$ . Peak assignment in Table 16.3.1.

TABLE 16.3.1. Identification of the main peaks in the chromatogram shown in Figure 16.3.1 for pyrolysis of maltitol at 900 °C

No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent pyrolysate
1	Carbon dioxide	4.30	44	124-38-9	8.31
2	Propene	4.55	42	115-07-1	1.37
3	Formaldehyde	4.73	30	50-00-0	<b>10.06</b>
4	1,3-Butadiene	5.33	54	106-99-0	0.44
5	Acetaldehyde	5.90	44	75-07-0	4.49
6	Furan	7.74	68	110-00-9	2.77
7	1,3-Cyclopentadiene	8.66	66	542-92-7	0.71
8	2-Propenal (acrolein)	8.81	56	107-02-8	2.68
9	Acetone	9.23	58	67-64-1	0.33
10	Butanal	9.78	72	123-72-8	3.17
11	2,3-Dihydrofuran	11.12	70	1191-99-7	0.15
12	2-Methylfuran	12.21	82	534-22-5	0.57
13	Methyl vinyl ketone	14.39	70	78-94-4	0.44
14	2,3-Butanedione (diacetyl)	14.66	86	431-03-8	0.53
15	Hydroxyacetaldehyde (glycol aldehyde)	17.97	60	141-46-8	7.36
16	2-Butenal	19.61	70	15798-64-8	0.20
17	2-Methyl-2-propenal	19.69	70	78-85-3	0.36
18	Acetic acid	20.24	60	64-19-7	0.14
19	Vinylfuran	21.05	94	1487-18-9	0.17
20	Ethyl-1-propenyl ether	22.52	86	928-55-2	0.49
21	1-Hydroxy-2-propanone (acetol)	22.67	74	116-09-6	2.76
22	3-Methylfuran	25.86	82	930-27-8	0.40
23	2-Propenoic acid methyl ester?	26.86	86	96-33-3	0.29
24	1,4-Dioxadiene	29.08	84	N/A	3.81
25	2-Oxopropionic acid methyl ester?	29.49	102	600-22-6	0.15
26	Butandial	29.84	86	638-37-9	0.93
27	Furancarboxaldehyde (furfural)	30.54	96	98-01-1	3.73
28	2-Propylfuran	31.00	110	4229-91-8	1.66
29	2-Furanmethanol	31.84	98	98-00-0	0.18
30	5-Methyl-2(3H)-furanone	32.21	98	591-12-8	0.15
31	Vinyl-2(3H)-furanone	32.65	110	N/A	0.10
32	Methylglyoxal+unknown	32.81	72	78-98-8	0.19
33	1-(2-furanyl)ethanone	33.31	110	1192-62-7	0.66
34	Dihydro-4-hydroxy-2(3H)-furanone	34.28	102	5469-16-9	1.33
35	2-Hydroxy-2-cyclopenten-1-one	34.68	98	10493-98-8	0.80
36	2-Cyclohexen-1-ol	35.54	98	822-67-3	0.19
37	5-methyl-2-furancarboxaldehyde	35.75	110	620-02-0	0.56
38	1,3-Benzenediol	35.07	110	108-46-3	0.13
39	5-Acetyldihydro-2(3H)-furanone	37.11	128	29393-32-6	0.15
40	6,8-Dioxabicyclo[3.2.1]octane	37.58	114	280-16-0	1.03
41	2-Hydroxy-3-methyl-2-cyclopenten-1-one (cyclotene)	38.11	112	80-71-7	0.40
42	Phenol	38.80	94	108-95-2	0.24

(Continued)

TABLE 16.3.1. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent pyrolysate
43	1,5-Hexadien-3-ol	38.96	98	924-41-4	0.30
44	2,5-dimethyl-4-hydroxy-3(2H)-furanone?	39.85	128	3658-77-3	0.14
45	3-Furancarboxylic acid methyl ester	41.01	126	13129-23-2	0.39
46	Unknown	41.15	116	N/A	0.16
47	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	42.79	144	28564-83-2	0.16
48	(Z)-penta-2,4-dienoic acid?	43.12	98	N/A	0.40
49	1-Hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one	45.82	144	113781-13-8	1.12
50	1,4:3,6-Dianhydro- $\alpha$ -D-glucopyranose	46.49	144	N/A	0.91
51	Unknown	47.20	144	N/A	0.13
52	5-(hydroxymethyl)-2-furancarboxaldehyde	47.77	126	67-47-0	1.20
53	1,4:3,6-Dianhydro-D-glucitol (isosorbide)	49.23	146	652-67-5	0.65
54	1,2-Cyclohexanediol?	49.50	116	1792-81-0	0.34
55	3-Hydroxy-6-(hydroxymethyl)-5H-6-hydropyran-4-one	50.06	144	N/A	2.50
56	Unknown	50.27	144	N/A	0.16
57	Unknown	53.84	128	N/A	0.16
58	1,6-Anhydro- $\beta$ -D-glucopyranose (levoglucosan)	56.95	162	498-07-7	<b>17.84</b>
59	Unknown	58.15	162	N/A	0.22
60	1,4-Anhydro-D-glucitol	59.36	164	N/A	3.00
61	Methyl-D-glucofuranoside?	59.65	164	N/A	1.57
62	1,6-Anhydro- $\beta$ -D-glucofuranose	60.08	162	7425-74-3	2.68
63	Anhydro sugar	60.53	162	N/A	1.40

Notes: Numbers in bold indicate the major pyrolysis constituents. Hydrogen, CO, methane, ethylene, and water not included.

compounds typical for glucose pyrolysis (e.g., a larger level of levoglucosan), and compounds typical for sorbitol (e.g., isosorbide). Maltitol pyrolysate composition is basically an average of the composition of the pyrolysates of the two molecular moieties (glucose and glucitol), such that little interaction appears to occur between these two parts during pyrolysis. This effect is very likely caused by the relatively weak ether bond between the sugar and the alcohol.

### Sugar acids

Sugar acids can be obtained either by the direct oxidation of a carbohydrate or by indirect methods such as the oxidation of a monosaccharide with specifically protected groups followed by the elimination of this protection. The main types of acids generated from carbohydrates are the following:

- Aldonic acids that can be generated by the direct oxidation of the aldehyde group into COOH group. The general formula of these compounds is  $\text{HOCH}_2-(\text{HC}(\text{OH}))_n-\text{COOH}$ . A typical example of aldonic acid is gluconic acid (2R,3S,4R,5R)-2,3,4,5,6-pentahydroxy-hexanoic acid. The formation of cyclic acetals is not possible for these compounds since no carbonyl group is available. Aldonic acids are typical hydroxy acids, and their pyrolysis is presented in Section 17.3 together with other hydroxy acids.

- Aldaric acids generated by the transformation of both the aldehyde group and of the terminal  $\text{CH}_2\text{OH}$  group in  $\text{COOH}$ . The general formula for these compounds is  $\text{HOOC}-(\text{HC}(\text{OH}))_n-\text{COOH}$ . A typical example in this group is the saccharic acid (glucaric acid) or (2S,3S,4S,5R)-2,3,4,5-tetrahydroxyhexandioic acid. The formation of cyclic acetals is not possible for these compounds, because no carbonyl group is available. Aldaric acids also are typical hydroxy acids, and their pyrolysis is presented in Section 17.3.
- Uronic acids generated by the transformation of the terminal  $\text{CH}_2\text{OH}$  group in  $\text{COOH}$ . The general formula is  $\text{HOOC}-(\text{HC}(\text{OH}))_n-\text{CHO}$  for these compounds. A typical example in this group is glucuronic acid or 3,4,5,6-tetrahydroxytetrahydropyran-2-carboxylic acid. Since the carbonyl group remains unaffected in uronic acids, they form cyclic acetals similar to the saccharide to which they are related. This is possible by modifying the carbonyl group into an internal acetal, and uronic acids are presented in this section.
- Saccharinic acids or 3-deoxyaldonic acids that are formed in strong basic media from carbohydrates. The reaction of formation of saccharinic acids plays a particularly important role in the pyrolysis of carbohydrates in the presence of TMAH when a thermo chemolysis and methylation process takes place (see reaction 16.1.12).
- Ketoaldonic acids with the general formula  $\text{HOCH}_2-(\text{HC}(\text{OH}))_n-\text{C}(\text{O})-\text{COOH}$  (also known as ulonic acids), which are also derivatives of certain sugars and can be generated by their oxidation with strong oxidants (e.g., chromic acid) in the presence of catalysts.
- Ascorbic acid, which is in fact a lactone that can ionize and has acidic properties. Pyrolysis of ascorbic acid is discussed in Section 19.3.

Only uronic acids have a chemical structure closely related to that of carbohydrates. Pyrolysis of a sample of D-glucuronic acid performed on 1.0 mg compound in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 700^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ , generates the pyrogram shown in Figure 16.3.2. Pyrolysis in identical conditions except for  $T_{\text{eq}} = 900^\circ\text{C}$  generates almost identical results. The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 16.3.2. The calculation of the mole percent was obtained based solely on peak areas.

As shown in Table 16.3.2, some of the compounds generated in pyrolysis of glucuronic acid are identical to those generated from glucose pyrolysis. These are small fragment molecules such as acetaldehyde, furan, furfural, etc. A few minor pyrolysate constituents are different, but they also consist of furan or pyran derivatives. The main reaction taking place during D-glucuronic acid pyrolysis is the

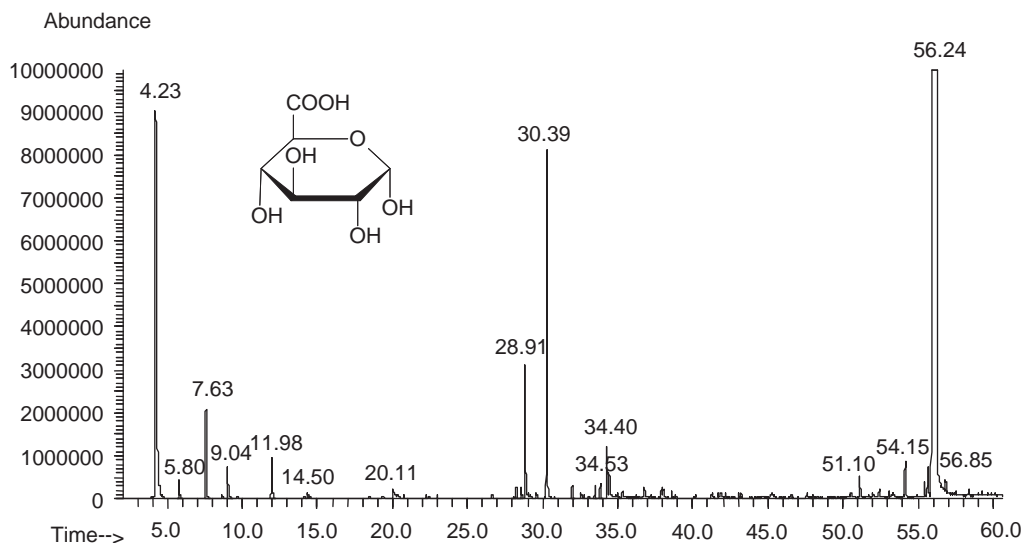


FIGURE 16.3.2. Pyrogram of D-glucuronic acid at  $700^\circ\text{C}$ . Peak assignment in Table 16.3.2.

TABLE 16.3.2. Identification of the main peaks in the chromatogram shown in Figure 16.3.2 for the pyrolysis of D-glucuronic acid at 700°C

No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent pyrolysate
1	Carbon dioxide*	4.23	44	124-38-9	<b>29.53</b>
2	Acetaldehyde*	5.80	44	75-07-0	0.71
3	Furan*	7.63	68	110-00-9	2.14
4	2-Propenal (acrolein)*	8.68	56	107-02-8	0.15
5	Acetone*	9.04	58	67-64-1	1.16
6	2-Methylfuran*	11.98	82	534-22-5	0.93
7	2,3-Butanedione (diacetyl)*	14.5	86	431-03-8	0.13
8	Acetic acid*	20.11	60	64-19-7	0.42
9	2(5H)-Furanone	28.27	84	497-23-4	0.19
10	2-Cyclopentandione*	28.60	98	3008-40-0	0.15
11	1,4-Dioxadiene*	28.91	84	N/A	2.58
12	Butanedial	29.60	86	638-37-9	0.14
13	Furancarboxaldehyde (furfural)*	30.39	96	98-01-1	4.90
14	5-Methyl-2(3H)-furanone*	31.98	98	591-12-8	0.17
15	Methylglyoxal+unknown*	32.58	72	78-98-8	0.10
16	2-Methylcyclopentene-1-one*	33.85	96	1120-73-6	0.19
17	Dihydro-3-methylene-2(3H)-furanone*	34.40	98	547-65-9	0.67
18	2-Hydroxy-2-cyclopenten-1-one*	34.53	98	10493-98-8	0.32
19	Benzaldehyde+unknown*	35.02	106	100-52-7	0.07
20	2-Methylenecyclopentanol*	35.33	98	20461-31-8	0.11
21	2-Hydroxy-3-methyl-2-cyclopenten-1-one*	37.94	112	80-71-7	0.17
22	2H-Pyran-2,6(3H)-dione	38.05	112	5926-95-4	0.18
23	Phenol*	38.60	94	108-95-2	0.09
24	3-Methylphenol (m-cresol)	41.31	108	108-39-4	0.12
25	1,3-Cyclopentandione	41.70	98	3859-41-4	0.11
26	Furylformate?	41.88	126	13493-97-5	0.09
27	5-Oxotetrahydrofuran-2-carboxylic acid methyl ester	42.20	144	21461-85-8	0.09
28	(3E)-4-(2-furyl)-3-buten-2-one	43.24	136	41438-24-8	0.06
29	3-Hydroxybenzaldehyde	51.10	122	100-83-4	0.41
30	Unknown	52.42	162	N/A	0.07
31	1-(2-Hydroxyphenyl)ethanone	53.10	136	118-93-4	0.06
32	Deoxy-glucuronic acid	54.15	176	N/A	0.38
33	Glucuronic acid?-lactone	55.44	176	N/A	0.12
34	Deoxy-glucuronic acid	55.65	176	N/A	0.31
35	Glucuronic acid 1,6-lactone	56.24	176	N/A	<b>52.54</b>
36	Unknown	56.85	192	N/A	0.19
37	Trihydroxyperhydropyran-2-carboxylic acid	58.38	178	N/A	0.06
38	3,5,7-Trihydroxy-2H-1-benzopyran-2-one	60.73	194	22065-07-2	0.07
39	Dihydroxydihydropyran-2-carboxylic acid	60.91	160	N/A	0.12

Notes: Numbers in bold indicate the major pyrolysis constituents.

Hydrogen, CO, methane, ethane, and water not included.

\*Compounds identical with those generated from the pyrolysis of glucose.

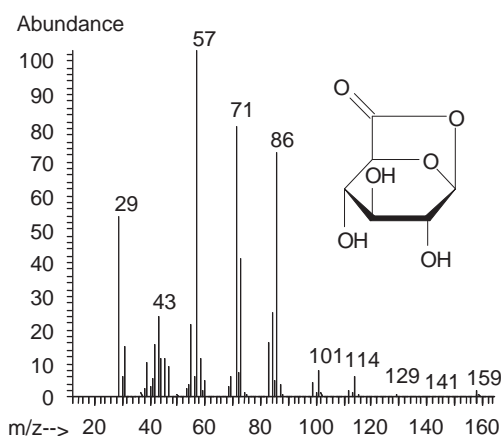
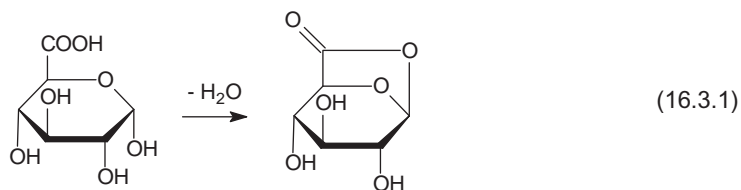


FIGURE 16.3.3. Mass spectrum of *D*-glucuronic acid-1,6-lactone ( $MW = 176$ .)

formation of a 1,6-lactone (2,3,4-trihydroxy-7,8-dioxabicyclo[3,2,1] octan-6-one) as shown in the reaction below:



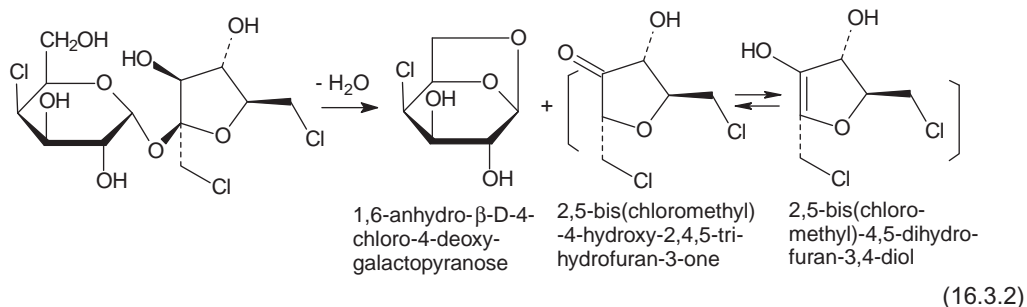
The reaction is similar to the formation of levoglucosan from glucose (see Section 16.1). The mass spectrum of *D*-glucuronic acid-1,6-lactone is given in Figure 16.3.3.

The GC/MS analysis of silylated pyrolysate shows in addition to the compounds listed in Table 16.3.2, low levels of undecomposed glucuronic acid and traces of a few disaccharide-type compounds.

### Halogenated sugars

Among halogenated sugars, sucralose or 1,6-dichloro-1,6-dideoxy- $\beta$ -*D*-fructofuranosyl-4-chloro-4-deoxy- $\alpha$ -*D*-galactopyranoside is of more interest, being a common sweetener. Pyrolysis of a sample of sucralose performed on 1.0 mg compound in a Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 700^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280^\circ\text{C}$ , generates the pyrogram shown in Figure 16.3.4. The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 16.3.3. The calculation of the mole percent was obtained based solely on peak areas.

As shown in Table 16.3.3, a number of compounds from sucralose pyrolysis are similar to those from other (non-chlorinated) carbohydrates. Several chlorinated compounds are also generated in the pyrolysate, including HCl, chloroacetaldehyde, chloropropanone, etc. The main pyrolysis product (in the conditions of experiment) is the formation of a chlorinated equivalent to levoglucosan from the pyrolysis of other sugars. The reaction is shown below:



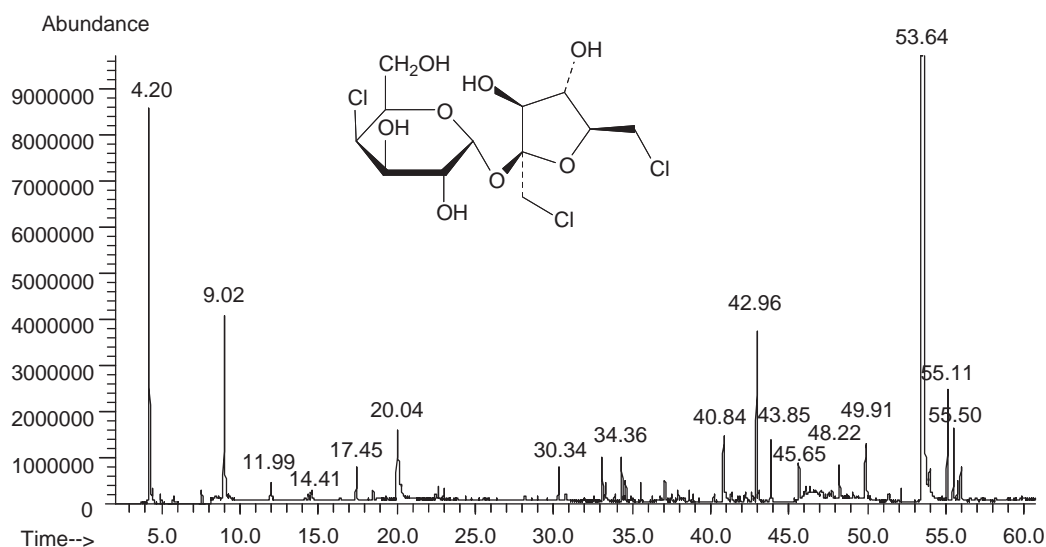


FIGURE 16.3.4. Pyrogram of 1 mg sucralose at 700°C.

TABLE 16.3.3. Identification of the main peaks in the chromatogram shown in Figure 16.3.4 for the pyrolysis of sucralose at 700°C

No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent pyrolysate
1	Carbon dioxide*	4.20	44	124-38-9	<b>20.78</b>
2	Propene	4.45	42	115-07-1	0.85
3	2-Methylpropene	4.96	56	115-11-7	0.33
4	Acetaldehyde*	5.8	44	75-07-0	0.27
5	Furan*	7.58	68	110-00-9	0.41
6	Hydrochloric acid	8.13 peak extended	36	7647-01-0	<b>8.68</b>
7	Acetone*	9.02	58	67-64-1	6.51
8	2-Methylfuran*	11.99	82	534-22-5	0.60
9	2,3-Butanedione (diacetyl)*	14.5	86	431-03-8	0.24
10	Chloroacetaldehyde	14.62	78	107-20-0	0.53
11	Benzene*	16.44	78	71-43-2	0.16
12	2-Chlorofuran	17.45	102	N/A	0.63
13	2,5-Dimethylfuran*	18.52	96	625-86-5	0.21
14	Acetic acid*	20.04	60	64-19-7	5.49
15	1-Chloro-2-propanone	22.70	92	78-95-5	0.28
16	Toluene*	23.02	92	108-88-3	0.21
17	Furancarboxaldehyde (furfural)*	30.34	96	98-01-1	0.66
18	1-(2-Furyl)ethanone*	33.12	110	1192-62-7	0.58
19	2,4-Pentanedione?	33.32	100	123-54-6	0.46
20	Dihydro-3-methylene-2(3H)-furanone	34.36	98	547-65-9	0.72
21	Unknown*	34.62	112	N/A	0.32
22	5-Methyl-2-furancarboxaldehyde*	35.57	110	620-02-0	0.32
23	Unknown*	37.11	110	N/A	0.27

TABLE 16.3.3. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent pyrolysate
24	2-Hydroxy-3-methyl-2-cyclopenten-1-one (cyclopentene)*	37.95	112	80-71-7	0.16
25	Phenol*	38.66	94	108-95-2	0.20
26	3-Furancarboxylic acid methyl ester*	40.84	126	13129-23-2	1.36
27	3-Methylphenol	41.37	108	108-39-4	0.31
28	Levogluconenone*	42.96	126	37112-31-5	2.06
29	Unknown	43.85	126	N/A	0.92
30	Unknown	48.22	144	N/A	0.48
31	Dianhydro sugar*?	49.91	144	N/A	1.07
32	4-Chloro-7,8-dioxabicyclo[3.2.1]octane-2,3-diol (1,6-anhydro- $\beta$ -D-4-chloro-4-deoxygalactopyranose)	53.65	180	N/A	<b>41.94</b>
33	2,5-Bis(chloromethyl)-4-hydroxy-2,4,5-trihydrofuran-3-one?	55.11	198	N/A	<b>0.82</b>
34	Unknown chlorinated sugar fragment	55.51	198	N/A	0.64
35	Unknown sugar related	55.74	?	N/A	~0.21
36	Unknown sugar related	55.97	?	N/A	~0.32

Notes: Numbers in bold indicate the major pyrolysis constituents.

Hydrogen, CO, methane, ethylene, and water not included.

\*Compounds identical in nature with those generated from the pyrolysis of glucose.

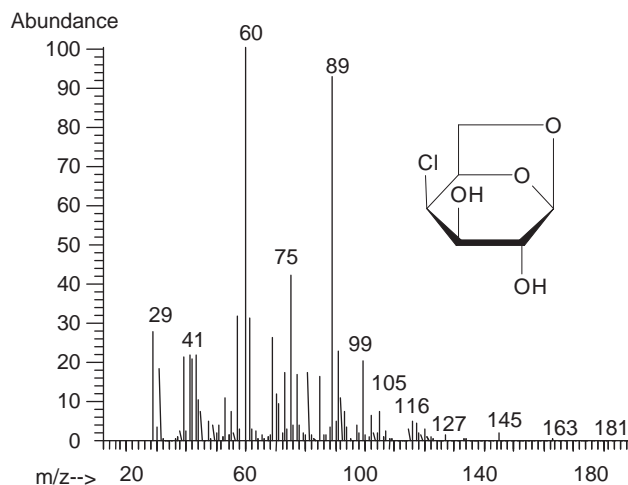


FIGURE 16.3.5. Mass spectrum of 1,6-anhydro- $\beta$ -D-4-chloro-4-deoxygalactopyranose (MW = 180).

The identification of 1,6-anhydro- $\beta$ -D-4-chloro-4-deoxygalactopyranose is more certain, while the structure of the other fragment is only tentative. The mass spectrum of 1,6-anhydro- $\beta$ -D-4-chloro-4-deoxygalactopyranose is shown in Figure 16.3.5. The mass spectrum of TMS derivative of 6-anhydro- $\beta$ -D-4-chloro-4-deoxygalactopyranose is shown in Figures 16.3.6. The TMS derivative of 2,5-bis-(chloromethyl)-4-hydroxy-2,4,5-trihydrofuran-3-one becomes the TMS derivative of 2,5-bis(chloromethyl)-4,5-dihydrofuran-3,4-diol and its spectrum is shown in Figure 16.3.7. This takes place as the ketone 2,5-bis(chloromethyl)-4-hydroxy-2,4,5-tri-hydrofuran-3-one is involved in a keto-enol equilibrium and the enol generates the TMS derivative [30].



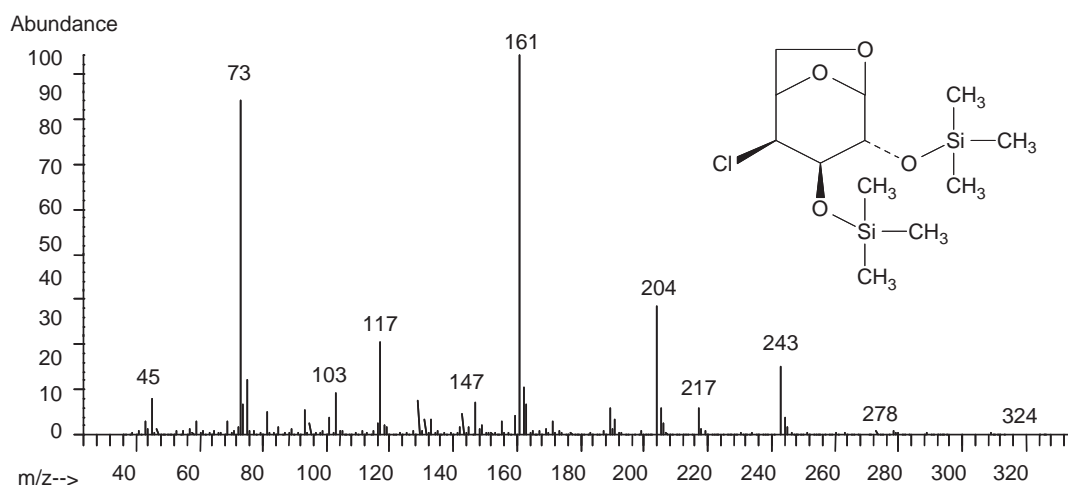


FIGURE 16.3.6. Mass spectrum of TMS derivative of 1,6-anhydro- $\beta$ -D-4-chloro-4-deoxygalactopyranose ( $MW = 324$ ).

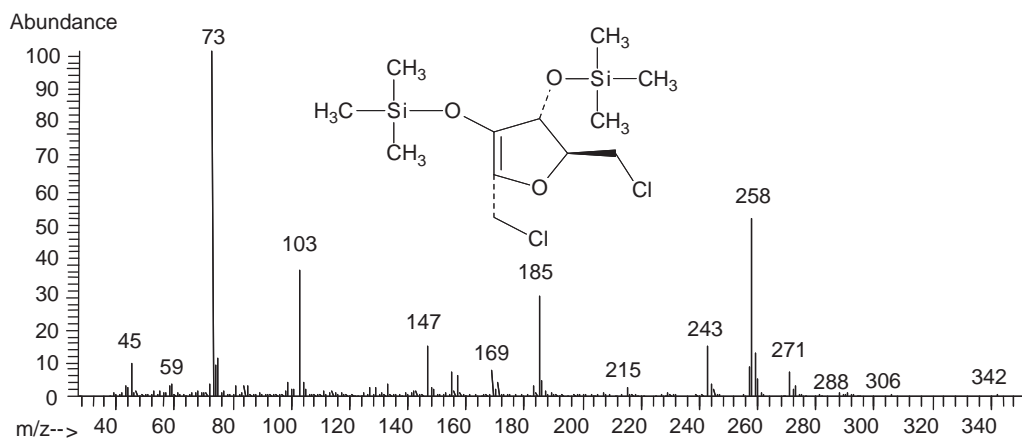


FIGURE 16.3.7. Mass spectrum of TMS derivative of 2,5-bis(chloromethyl)-4,5-dihydrofuran-3,4-diol ( $MW = 342$ ).

Analysis of sucralose pyrolysate indicates that compounds similar to those generated from other sugars also are produced from the pyrolysis of this compound. The elimination of HCl from the molecule is in many respects similar to the elimination of  $H_2O$  from simple sugar molecules.

### Ethers and silyl ethers of saccharides

Ethers and silyl ethers of carbohydrates are somewhat more stable to higher temperatures compared to the unmodified compounds. Pyrolysis of these compounds is reported in the literature only in relation with their formation by pyrolysis in the presence of a derivatization reagent such as TMAH [5,23,31,32] or hexamethyldisilazane [23]. The resulting compounds (methyl ethers of TMS ethers) are stable in the conditions in which they are generated (700 °C for the TMAH thermo chemolysis/methylation).

## Glycosides

Glycosides are compounds frequently found in nature (e.g., [33–35]) (glycosides formed with glucose are named glucosides). Examples of glucosides are salicin or 2-(hydroxymethyl)phenyl- $\beta$ -D-glucopyranoside (related to aspirin) found in willow bark, naringin, a flavonoid glycoside that gives the bitter taste to grapefruit, neohesperidin dihydrochalcone, which is an artificial sweetener derived from bitter neohesperidin found in citrus juices, and rutin, a flavonoid glycoside also known as vitamin P1. Among other natural glycosides are those formed with 27-carbon steroids or with 30-carbon triterpenes that form the group of saponins. This group includes the cardiac steroids, glycyrrhizin, which is a glycoside (with a sugar acid) of glycyrrhetic acid and is found in licorice root, and many other plant glycosides.

Pyrolysis of glycosides typically gives a mixture of compounds, some resulting from the saccharide and some from the aglycon moieties, with little interaction of the two parts of the molecule. This effect, also seen, for example, in disaccharides or in compounds part carbohydrate part polyol (maltitol), is caused by the relatively weak ether bond between the sugar and the aglycon. The glycosidic bond is cleaved faster than other parts of the molecule and generates fragments that undergo further pyrolytic decompositions.

An example of a glycoside pyrolysis is given below for neohesperidin dihydrochalcone. From the name of this compound, 2-O-(6-deoxy-2-O-{3,5-dihydroxy-4-[3-(3-hydroxy-4-methoxyphenyl)propanoyl]phenyl}- $\alpha$ -L-mannopyranosyl)- $\beta$ -D-glucopyranose, it can be seen the aglycon part (chalcone derivative) as well as the sugar moiety (rhamnoglucose). The compound is closely related to naringin (4',5,7-trihydroxyflavanone-7-rhamnoglucoside).

Pyrolysis of a sample of 1.0 mg neohesperidin dihydrochalcone, in a Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280^\circ\text{C}$ , generates the pyrogram shown in Figure 16.3.8. The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 16.3.4. The calculation of the mole percent was obtained based solely on peak areas.

Pyrolysis products listed in Table 16.3.4 can be grouped easily into fragments resulting from the sugar (furan derivatives, 6-methyl-5,7-dioxabicyclo[2.2.1]heptan-2-one, levoglucosenone, levoglucosan, etc.) and those resulting from the aglycon (most phenol derivatives) including 4-(4-hydroxy-3-methoxyphenyl)butan-2-one. Even some of the compounds resulting from the rhamnose fragment (5-methyl-6,7-dioxabicyclo[2.2.1]-heptan-2-one) and those from the glucose fragment (levoglucosenone, levoglucosan) can be identified. A “model” reaction for the formation of some of the main pyrolysis

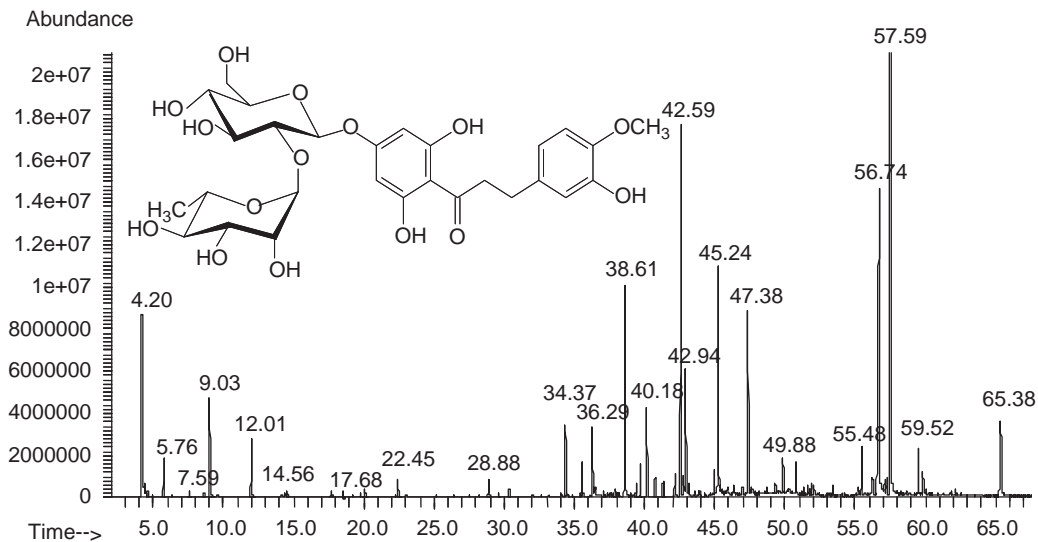


FIGURE 16.3.8. Pyrogram of neohesperidin dihydrochalcone at  $900^\circ\text{C}$ .

TABLE 16.3.4. Identification of the main peaks in the chromatogram shown in Figure 16.3.8 for the pyrolysis of neohesperidin dihydrochalcone at 900 °C

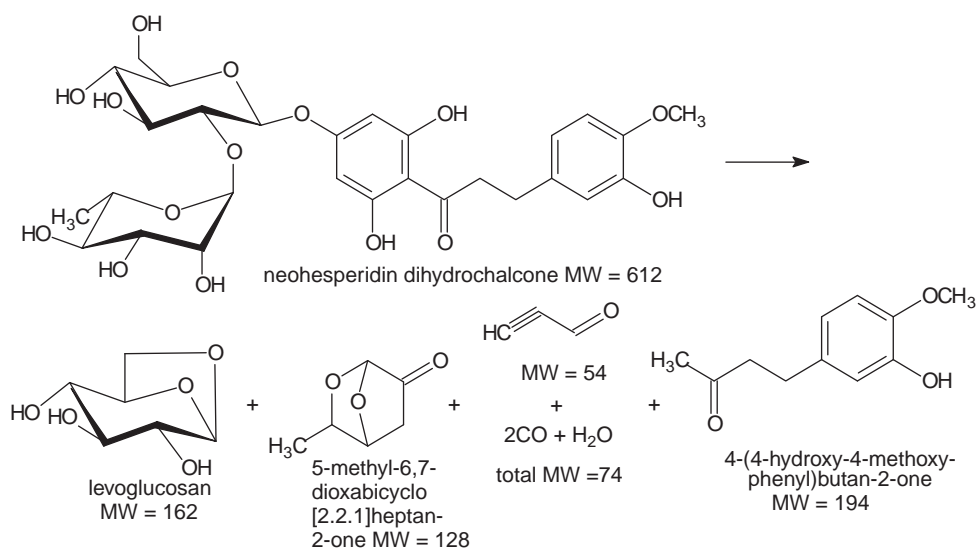
No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent pyrolysate
1	Carbon dioxide	4.21	44	124-38-9	<b>15.68</b>
2	Propene	4.45	42	115-07-1	1.08
3	Formaldehyde	4.63	30	50-00-0	0.53
4	Propynal	5.29	54	624-67-9	Trace
5	Acetaldehyde	5.76	44	75-07-0	2.02
6	Methanol	6.34	32	67-56-1	0.20
7	Furan	7.59	68	110-00-9	0.23
8	Propanal	8.65	58	123-38-6	0.20
9	Acetone	9.03	58	67-64-1	5.19
10	2-Methylfuran	12.01	82	534-22-5	2.15
11	2,3-Butanedione (diacetyl)	14.56	86	431-03-8	0.27
12	Hydroxyacetaldehyde (glycol aldehyde)	17.68	60	141-46-8	0.37
13	2,5-Dimethylfuran	18.54	96	625-86-5	0.19
14	Acetic acid	20.03	60	64-19-7	0.82
15	1-Hydroxy-2-propanone (acetol)	22.45	74	116-09-6	0.65
16	1,4-Dioxadiene	28.88	84	N/A	0.62
17	2,5-Furandione	29.62	98	N/A	0.11
18	Furancarboxaldehyde (furfural)	30.38	96	98-01-1	0.21
19	Dihydro-3-methylene-2(3H)-furanone	34.37	98	547-65-9	1.65
20	5-Methyl-2-furancarboxaldehyde	35.58	110	620-02-0	0.66
21	Unknown	36.29	128	N/A	1.44
22	3,5-Dimethyl-2,4(3H,5H)-furandione	36.49	128	5460-81-1	0.17
23	Resorcinol	37.12	110	108-46-3	0.10
24	2-Hydroxy-3-methyl-2-cyclopenten-1-one (cyclovene)	37.96	112	80-71-7	0.16
25	5-Methyl-6,7-dioxabicyclo[2.2.1]heptan-2-one	38.61	128	N/A	<b>4.31</b>
26	Isomaltol	39.41	126	3420-59-5	0.32
27	2-Methoxyphenol+unknown	39.70	124	90-05-1	0.62
28	Unknown from rhamnose	40.18	102	N/A	2.41
29	Unknown	40.76	144	N/A	0.33
30	Maltol	41.18	126	118-71-8	0.05
31	4-Methylphenol	41.31	108	106-44-5	0.26
32	3-Methylphenol	41.36	108	108-39-4	0.34
33	Unknown from sugar	42.17	128	N/A	0.63
34	2-Methoxy-5-methylphenol	42.59	138	1195-09-1	6.36
35	2,4-Dimethylphenol	42.81	122	105-67-9	0.60
36	Levogluconone	42.94	126	37112-31-5	3.48
37	3,5-Dihydroxy-2-methyl-4H-pyran-4-one (hydroxymaltol)	43.15	142	1073-96-7	0.33
38	Unknown	44.99	128	N/A	0.50
39	4-Ethyl-2-methoxyphenol	45.24	152	2785-89-9	3.81
40	1,4:3,6-Dianhydro- $\alpha$ -D-glucopyranose	46.33	144	N/A	0.15
41	Unknown	46.97	180	N/A	0.20
42	2-Methoxy-4-vinylphenol	47.38	150	7786-61-0	2.87
43	2',4'-Dihydroxy-3'-methylacetophenone+unknown	47.62	166	10139-84-1	0.04
44	Resorcinol monoacetate	48.73	152	102-29-4	0.12

TABLE 16.3.4. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent pyrolysate
45	Mixture	49.34	164	N/A	0.18
46	6-(Hydroxymethyl)-2-methyl-2H-3,5,6-trihydropyran-4-one	49.88	144	N/A	0.70
47	4-(1,2-Propandienyl)-guaiacol	50.79	162	N/A	0.67
48	1-(2,6-Dihydroxyphenyl)butan-1-one	51.20	180	N/A	0.06
49	Unknown aromatic compound	51.36	180	N/A	0.09
50	Unknown	51.61	180	N/A	0.13
51	2-Ethyl-1,4-benzodioxin?	51.87	162	27549-01-5	0.17
52	4-(4-Methoxyphenyl)-2-butanone	52.09	178	104-20-1	0.15
53	Anhydro sugar (from rhamnose?)	53.45	146	N/A	0.23
54	1-(4-Hydroxy-3-methoxyphenyl) ethanone	55.28	166	498-02-2	0.13
55	4-Hydroxy-2-methoxycinnamaldehyde	55.48	178	127321-19-1	0.63
56	4-(4-Hydroxyphenyl)-2-butanone	56.26	164	5471-51-2	0.30
57	1,6-Anhydro- $\beta$ -D-glucopyranose (levoglucosan)	56.75	162	498-07-7	<b>11.04</b>
58	Ethylhomovanillate?	57.13	210	60563-13-5	0.21
59	3,4-Methylenedioxyphenyl acetone	57.27	178	4676-39-5	0.21
60	4-(4-Hydroxy-3-methoxyphenyl)butan-2-one	57.59	194	122-48-5	<b>19.44</b>
61	Unknown	58.66	192	N/A	0.06
62	5-Hydroxy-6-methoxy-1-indanone	59.52	178	127933-78-4	0.69
63	1,6-Anhydro- $\beta$ -D-glucofuranose	59.86	162	7425-74-3	0.45
64	4,5-Dimethoxy-2-(2-propenyl)phenol?	60.09	194	N/A	0.07
65	1-(4-Methoxymethyl-2,6-dimethylphenyl)ethanone	62.18	192	1000202-02-2	0.11
66	6-(3-Hydroxy-4-methoxyphenyl)hexane-2,4-dione?	65.38	236	N/A	1.84

Notes: Numbers in bold indicate the major pyrolysis constituents. Hydrogen, CO, methane, ethane, and water not included.

products from neohesperidin dihydrochalcone is shown below (the sum of masses of fragments equals that of parent molecule):



(16.3.3)

Further pyrolysis of the intermediate compounds generated in reaction 16.3.3 as well as other pyrolysis products generated directly from the parent molecule lead to a complex pyrolysate composition. Char is also formed during pyrolysis as well as a considerable amount of  $\text{CO}_2$ , which shows that the reaction model 16.3.3 is far from complete.

Another example of the pyrolysis of a glycoside is that of rutin. The compound is quercetin-3-O- $\beta$ -D-glucose- $\alpha$ -L-rhamnose or 3-[[6-O-(6-deoxy- $\alpha$ -L-mannopyranosyl)- $\beta$ -D-glucopyranosyl]oxy]-2-(3,4-dihydroxyphenyl)-5,7-dihydroxy-4H-1-benzopyran-3-one. Pyrolysis of a sample of 1.0 mg rutin, in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ , generates the pyrogram shown in Figure 16.3.9. The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 16.3.5. The calculation of the mole percent was obtained based solely on peak areas.

Typical for a glycoside, the peaks in the pyrogram of rutin can be related to the peaks resulting from the pyrolysis of rutinose (see Table 16.2.1) or even glucose (see Table 16.1.2) and of quercetin (see Section 21.1). Some free quercetin is also present in the pyrolysate of rutin, but it can be detected only in the silylated pyrolysate. Pyrolysis of rutin also produces a considerable amount of char.

The pyrolysates of glycosides are frequently similar in composition with that of a mixture of the pyrolysis products of the sugar and of the aglycon. This was shown in the previous two examples for neohesperidin dihydrochalcone and also for rutin. The same pattern is seen during the pyrolysis of anthocyanins, where the pyrolysate is made from a mixture of compounds resulting from the sugar pyrolysis and from the anthocyanidin pyrolysis.

For the glycosides with a thermally stable aglycon, the capability of releasing the aglycon upon heating has been investigated with the purpose of developing nonvolatile flavor precursors. These compounds are intended to release the flavor only when heated, for example during cigarette smoking. A typical example of this type of glycoside is menthyl glucoside (menthyl- $\beta$ -D-glucopyranoside) [36]. The heating of this compound between ambient temperature to  $500^\circ\text{C}$  at a heating rate of  $10^\circ\text{C/min}$  showed that at  $200^\circ\text{C}$  the compound does not decompose, and between  $250^\circ\text{C}$  and  $300^\circ\text{C}$  the decomposition takes place mainly with the formation of menthol. At  $400^\circ\text{C}$ , besides menthol, various by-products generated mainly from the glucose moiety are produced. The formation of the unmodified aglycon from the pyrolysis of a glucoside is still dependent on the stability of the resulting compound. For some compounds, the first stage of decomposition reaction affects the aglycon molecule and not the sugar. A comparison of main pyrolysis reactions for menthyl glucoside and phenylethanol glucoside is shown

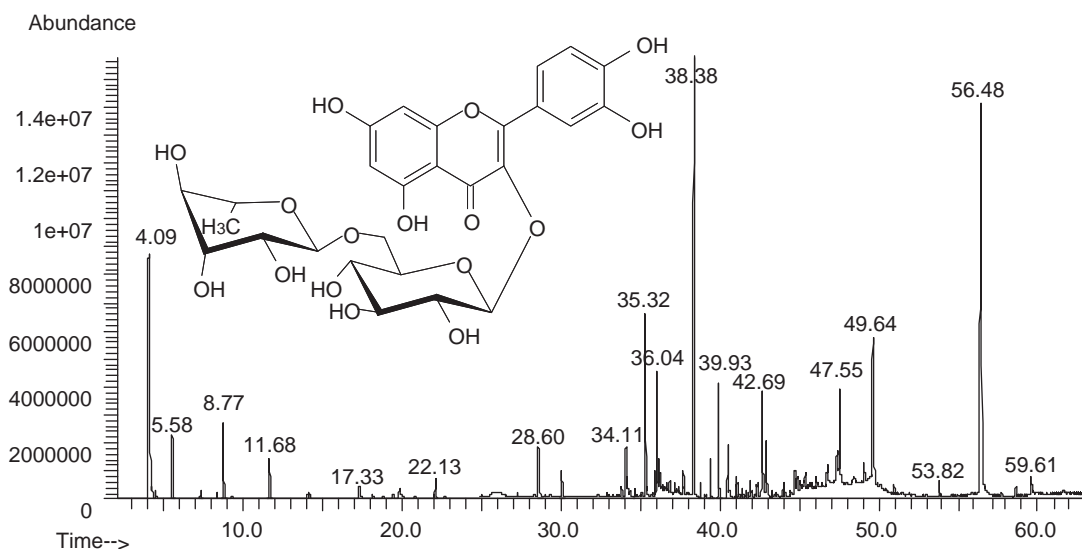


FIGURE 16.3.9. Pyrogram of rutin obtained at  $900^\circ\text{C}$ . Peak assignment in Table 16.3.5.

TABLE 16.3.5. *Identification of the main peaks in the chromatogram shown in Figure 16.3.9 for the pyrolysis of rutin at 900°C*

No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent
1	Carbon dioxide	4.09	44	124-38-9	24.74
2	Propene	4.30	42	115-07-1	0.86
3	Formaldehyde	4.50	30	50-00-0	0.75
4	Acetaldehyde	5.58	44	75-07-0	2.55
5	Furan	7.36	68	110-00-9	0.30
6	Propanal	8.38	58	123-38-6	0.32
7	Acetone	8.77	58	67-64-1	3.23
8	2-Methylfuran	11.68	82	534-22-5	1.35
9	Methyl vinyl ketone	13.81	70	78-94-4	0.12
10	2,3-Butanedione (diacetyl)	14.07	86	431-03-8	0.09
11	2-Butenone	14.19	72	78-93-3	0.36
12	Hydroxyacetaldehyde (glycol aldehyde)	17.33	60	141-46-8	0.96
13	2,5-Dimethylfuran	18.20	96	625-86-5	0.41
14	2-Methyl-3-buten-2-one	18.85	84	814-78-8	0.47
15	Acetic acid	19.87	60	64-19-7	1.11
16	Ethyl-1-propenyl ether	22.00	86	928-55-2	0.44
17	1-Hydroxy-2-propanone (acetol)	22.13	74	116-09-6	0.75
18	2,4-Pentandione	26.12	100	123-54-6	0.48
19	1,4-dioxadiene	28.60	84	N/A	1.69
20	Furancarboxaldehyde (furfural)	30.08	96	98-01-1	0.69
21	Dihydro-4-hydroxy-2(3H)-furanone	33.84	102	5469-16-9	0.36
22	Dihydro-3-methylene-2(3H)-furanone	34.11	98	547-65-9	2.10
23	5,6-Dihydro-4-methyl-2H-pyran-2-one	34.19	112	2381-87-5	0.41
24	1-Methyl-7-oxabicyclo[4.1.0]heptane	34.64	112	1713-33-3	0.41
25	6-Methylcyclohex-2-en-1-ol?	35.11	112	N/A	0.28
26	5-Methyl-2-furancarboxaldehyde	35.32	110	620-02-0	3.74
27	3-Methyl-1,2-cyclopentanedione	35.43	112	765-70-8	0.18
28	Unknown	35.91	112	N/A	0.53
29	3-Acetyldihydro-2(3H)-furanone	36.04	128	517-23-7	3.75
30	Tetrahydro-3,6-dimethyl-2H-pyran-2-one	36.23	128	3720-22-7	0.35
31	Unknown	36.86	110	N/A	0.51
32	2-Hydroxy-3-methyl-2-cyclopenten-1-one (cyclotene)	37.72	112	80-71-7	1.03
33	3-Hydroxy-5-methyl-5,6-dihydroxypyran-4-one	38.37	128	N/A	9.47
34	2,5-Dimethyl-4-hydroxy-3(2H)-furanone	39.44	128	3658-77-3	0.68
35	Unknown	39.93	128	N/A	2.21

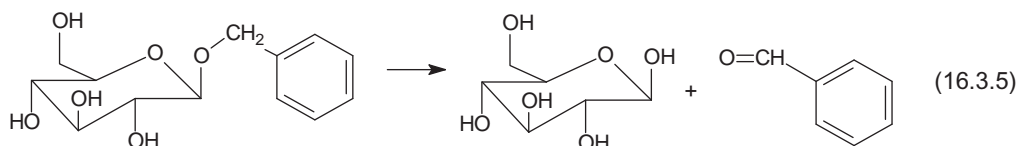
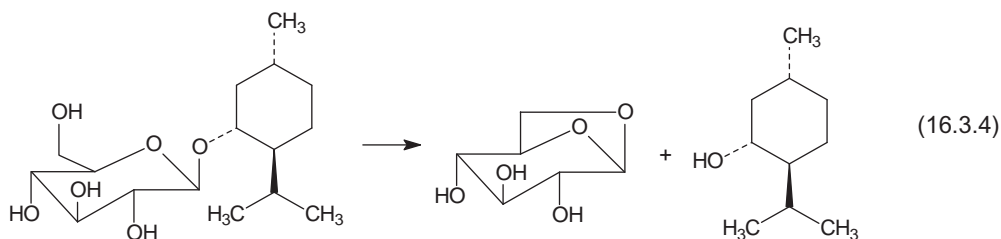
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TABLE 16.3.5. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent
36	Anhydro sugar from rhamnose	40.52	144	N/A	1.10
37	4-Methylphenol ( <i>p</i> -cresol)	41.08	108	106-44-5	0.88
38	1,3-Benzodioxol-2-one	41.40	136	2171-74-6	0.16
39	Anhydro sugar from rhamnose	42.39	144	N/A	0.68
40	Anhydro sugar from rhamnose	42.69	144	N/A	2.47
41	3,5-Dihydroxy-2-methyl-4H-pyran-4-one (hydroxymaltol)	42.94	142	1073-96-7	1.31
42	Dianhydromannitol	44.02	146	N/A	0.34
43	Unknown	44.75	128	N/A	0.53
44	4,7-Dihydro-1,3-isobenzofurandione	44.88	150	4773-89-1	0.41
45	2-Propoxyphenol	46.79	152	6280-96-2	0.75
46	1-(2-Hydroxy-6-methoxyphenyl)ethanone?	47.39	166	703-23-1	1.11
47	1,2-Benzenediol (catechol)	47.55	110	120-80-9	2.25
48	6-Hydroxy-4-methoxy-2,3-dimethylbenzaldehyde	49.09	180	34883-12-0	1.71
49	4-Methyl-1,2-benzenediol in mix	49.64	124	452-86-8	5.44
50	1,3-Benzenediol (resorcinol)	50.99	110	108-46-3	0.27
51	2,4-Dihydroxybenzeneacetic acid?	53.82	168	N/A	0.30
52	1,6-Anhydro- $\beta$ -D-glucopyranose (levoglucosan)	56.47	162	498-07-7	12.11
53	2,5-Dihydroxybenzeneacetic acid?	58.65	168	451-13-8	0.14
54	1,6-Anhydro- $\alpha$ -D-galactofuranose	59.61	162	N/A	0.34

Hydrogen, CO, methane, ethane, and water not included.

in reactions 16.3.4 and 16.3.5, respectively:



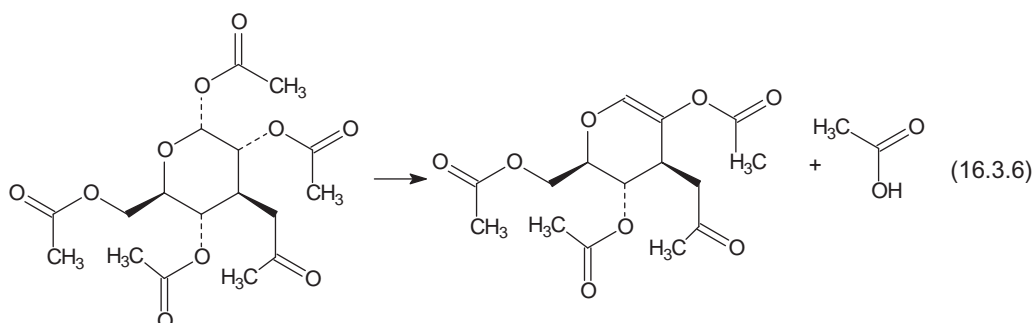
Further decomposition of the sugar and of the aglycon is not uncommon and depends on the pyrolysis conditions ( $T_{\text{eq}}$  in particular).

### Sugar esters

Sugar esters are compounds resulting from the esterification reaction between a carbohydrate (acting as an alcohol) and an organic or inorganic acid. A wide range of compounds can be obtained as esters even considering one type of acyl group. The acyl can be attached to a different number of OH groups and at different positions in the carbohydrate.

Pyrolysis of glucose pentaacetate in Type 1 Experiment conditions as described in Section 4.6, at  $T_{eq} = 700^{\circ}\text{C}$ ,  $\beta = 10^{\circ}\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280^{\circ}\text{C}$ , lead to only about 15% decomposition of the parent molecule, the rest of it transferring intact to the GC/MS system. Some of the sample may have been transferred before reaching the nominal  $T_{eq}$  value, being vaporized without decomposition and transferred out of the heating zone.

The decomposition products of glucose pentaacetate include acetic acid, acetic anhydride, and compounds such as 1,5-anhydro-D-arabino-hex-1-enitol tetraacetate:



The elimination of the acetic acid molecule can take place from positions other than C1, leading to analogous compounds.

The carbohydrates only partially esterified are less stable to heating. The pyrolysis products generated from these esters include the free acids and sugar decomposition products. The amount of acid released from sugar esters depends on the number of esterified OH groups, the position of esterification, and the heating temperature. The compounds with a high degree of esterification have the tendency to generate molecules that retain the acyl group, such that they do not yield the highest level of free acid [37].

Among the inorganic esters of carbohydrates, glucose-6-phosphate is probably the most important compound since it is involved in cell metabolism. Besides the formation of  $\text{H}_3\text{PO}_4$ , pyrolysis of glucose-6-phosphate is not expected to generate fragments different from those generated from glucose (see Section 19.2).

### Amino sugars

The replacement of the OH group from C2 of glucose with an  $\text{NH}_2$  group leads to the formation of 2-amino-2-deoxy-D-glucose (glucosamine). Glucosamine is a precursor in the synthesis of glycosylated proteins and is the building block for chitosan and (in acetylated form) for chitin. The amino group, having a basic character, can form salts with various acids. Pyrolysis at  $900^{\circ}\text{C}$  of glucosamine in its salt form with HCl generates three types of compounds. The first type of compounds includes small molecules that are similar to those generated in glucose pyrolysis. These molecules include  $\text{CO}_2$ , aldehydes, furans, and other small molecules. Levoglucosenone is also present in the pyrolysate (at about 0.2%), but levoglucosan is absent. No aminated equivalent of levoglucosan was detected in the pyrolysate. The second type of compounds is nitrogen containing. They include acetonitrile, propanenitrile, and low levels of alkyl pyridines and pyrazines. The third group of compounds includes a few chlorinated compounds. Besides HCl that was expected in the pyrolysate, compounds such as methylene chloride and 3-chloro-2-cyclopenten-1-one were also detected. This indicates that the



formation of an excess of HCl during pyrolysis leads to the interactions of this compound with organic fragments and the formation of organo-chlorine compounds.

N-Acetyl-D-glucosamine (GlcNAc) is an important amino sugar in the bacterial cell wall, as a component of peptidoglycans. In these polymers, N-acetyl-D-glucosamine is typically connected on one side with other sugars and on the other side to 2-acetamido-2-deoxymuramic acid and further to the amino acids in a protein chain (see e.g., [2]). From a chemical point of view, N-acetyl-D-glucosamine is an amide of acetic acid with 2-amino-2-deoxy-D-glucose. Having a large sugar moiety, it is interesting to compare its pyrolysis with other sugars. For this purpose, a sample of 1.0 mg N-acetyl-D-glucosamine was pyrolyzed in a Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900^{\circ}\text{C}$ ,  $\beta = 10^{\circ}\text{C/ms}$ ,  $\text{THT} = 10\text{ s}$ , and housing temperature  $T_{\text{hou}} = 280^{\circ}\text{C}$ . The analysis of pyrolysate was done by GC/MS under conditions given in Table 4.6.1. The pyrogram is shown in Figure 16.3.10, and the compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 16.3.6. The calculation of the mole percent was obtained based solely on peak areas.

The compounds from Table 16.3.6 indicate that the pyrolysis of N-acetylglucosamine is in many respects similar to that of other sugars. The formation of small molecules including  $\text{CO}_2$ , ( $\text{H}_2\text{O}$  not shown in the table), small aldehydes and ketones, and furan derivatives is expected. However, the levels of furfural and 5-hydroxymethylfurfural are much lower than those for typical carbohydrates. Small molecules containing nitrogen also are generated, such as several nitriles. Acetic acid and acetamide are found in large proportions in the pyrolysate. Also, 3-acetamidofuran is present in the pyrolysate. One interesting reaction generating oxazoles derivatives also occur during pyrolysis. The first step of this reaction can be written as follows:

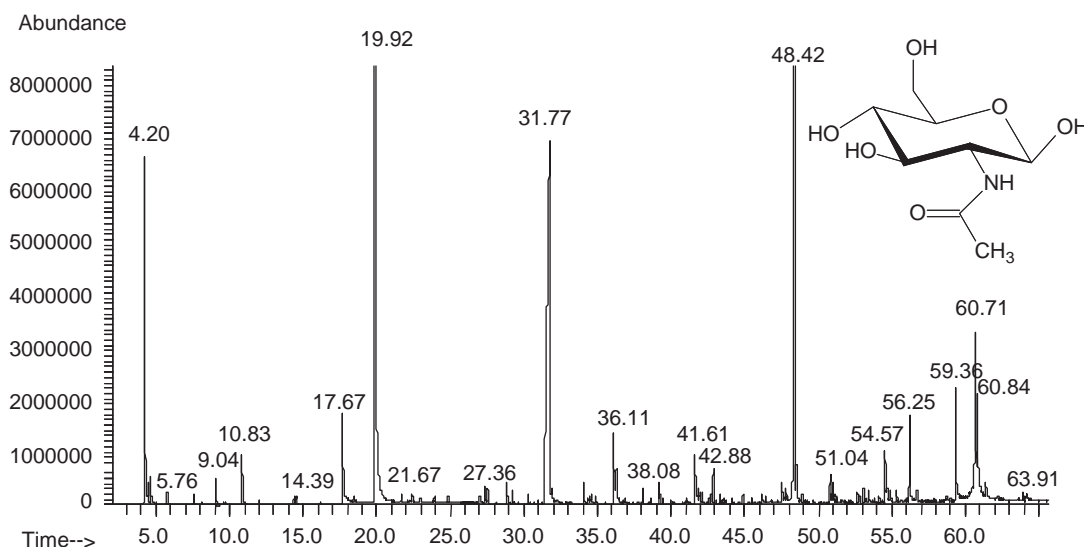
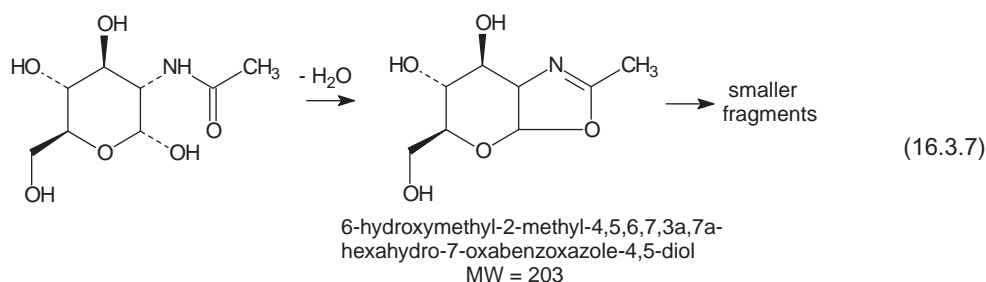


FIGURE 16.3.10. Pyrogram of 1 mg N-acetyl-D-glucosamine at  $900^{\circ}\text{C}$ . Peak identifications by their retention times given in Table 16.3.6.

TABLE 16.3.6. Identification of the main peaks in the chromatogram shown in Figure 16.3.10 for the pyrolysis of *N*-acetyl-*D*-glucosamine at 900°C

No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent pyrolysate
1	Carbon dioxide	4.20	44	124-38-9	<b>10.16</b>
2	Cyclopropane	4.47	42	75-19-4	0.75
3	Formaldehyde	4.63	30	50-00-0	1.37
4	Acetaldehyde	5.76	44	75-07-0	0.35
5	Furan	7.58	68	110-00-9	0.07
6	2-Propenal (acrolein)	8.64	56	107-02-8	0.20
7	Acetone	9.04	58	67-64-1	0.66
8	Acetonitrile	10.83	41	75-05-8	2.33
9	2-Methylfuran	11.97	82	534-22-5	0.05
10	2,3-Butanedione (diacetyl)	14.39	86	431-03-8	0.13
11	2-Butanone	14.53	72	78-93-3	0.17
12	Propanenitrile	16.20	55	107-12-0	0.08
13	Benzene	16.35	78	71-43-2	0.06
14	2-Methyloxazole	16.61	83	N/A	0.05
15	Hydroxyacetaldehyde (glycol aldehyde)	17.68	60	141-46-8	3.26
16	2,5-Dimethylfuran	18.50	96	625-86-5	0.06
17	Acetic acid	19.92	46	64-17-5	<b>34.07</b>
18	2,4-Dimethyloxazole	21.68	97	7208-05-1	0.09
19	1-Hydroxy-2-propanone (acetol)	22.43	74	116-09-6	0.11
20	Toluene	22.99	92	108-88-3	0.07
21	Pyridine	23.94	79	110-86-1	0.12
22	Acetic acid anhydride	24.87	102	108-24-7	0.07
23	2-Methylpyridine	26.99	93	109-06-8	0.14
24	Acetic acid methyl ester	27.36	74	79-20-9	0.29
25	Unknown	27.55	111	N/A	0.11
26	1H-Pyrrole	27.60	67	109-97-7	0.21
27	Ethylbenzene	28.16	106	100-41-4	0.04
28	3,3'-Oxybisoropropanenitrile	28.84	124	1656-48-0	0.29
29	Pyruvic acid methyl ester	29.26	102	600-22-6	0.14
30	Furancarboxaldehyde (furfural)	30.31	96	98-01-1	0.12
31	Acetamide	31.77	59	60-35-5	<b>26.76</b>
32	1-Acetyloxy-2-propanone	31.90	116	592-20-1	0.22
33	Dihydro-4-hydroxy-2(3H)-furanone	34.08	102	5469-16-9	0.31
34	2-Hydroxy-2-cyclopenten-1-one	34.50	98	10493-98-8	0.10
35	N-Acetylpyrrole	34.85	109	N/A	0.13
36	5-Ethyl-2,4-dimethyl-1,3-oxazole	36.11	125	N/A	0.92
37	2,4,5-Trimethyl-1,3-oxazoline	36.29	113	N/A	0.41
38	N-Acetylacetamide	38.08	101	625-77-4	0.20
39	Phenol	38.59	94	108-95-2	0.07
40	2-Methyl-4-butyloxazole	39.17	139	N/A	0.13
41	1H-Pyrrole-2-carboxaldehyde	39.25	95	1003-29-8	0.10

(Continued)

TABLE 16.3.6. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Moles percent pyrolysate
42	2-Methylbenzoxazole	41.02	133	95-21-6	0.01
43	1-(1H-Pyrrol-2-yl)ethanone	40.00	109	1072-83-9	0.04
44	3,4-Dimethyl-2-propyloxazole	41.01	139	53833-32-2	0.03
45	Acetamidoacetaldehyde	41.61	101	64790-08-5	1.07
46	Unknown	41.83	133	N/A	0.16
47	Oxazole derivative?	41.95	153	N/A	0.10
48	Unknown	42.15	133	N/A	0.15
49	Unknown	42.60	141	N/A	0.06
50	5-Methyl-2(1H)-pyridinone	42.75	109	1003-68-5	0.12
51	2-Furanmethanol+unknown	42.88	98	98-00-0	0.38
52	2-Pyridinmethanol acetate	43.32	151	1007-49-4	0.07
53	6-Methyl-2(1H)-pyridinone	44.15	109	3279-76-3	0.06
54	1,2-Dihydro-6-methyl-2-oxo-3-Pyridincarboxaldehyde	44.90	137	784440-89-8	0.09
55	Unknown	46.19	151	N/A	0.08
56	2,4,4-Trimethyl-2-enolide	46.43	126	4182-41-6	0.07
57	5-(Hydroxymethyl)-2-furancarboxaldehyde	47.55	126	67-47-0	0.24
58	Unknown	47.84	139	N/A	0.09
59	3-Acetamidofuran	48.42	125	59445-85-1	<b>6.32</b>
60	1-Acetamidobicyclo[3.2.0]heptan-2-one	48.54	167	N/A	0.23
61	Pyridin-2,6-diol, diacetate?	50.83	195	N/A	0.16
62	2-Acetamido-2-deoxyglucono-1,4-lactone?	51.04	219	N/A	0.11
63	Unknown	52.83	149	N/A	0.07
64	Unknown	53.10	169	N/A	0.11
65	N-(2,4-Dihydroxyphenyl)acetamide	54.57	167	71516-07-9	0.36
66	Unknown	54.72	128	N/A	0.20
67	Unknown	54.93	152	N/A	0.11
68	6-(Hydroxymethyl)-2-methyl-4,5,6,7,3a,7a-hexahydro-7-oxabenzoxazole-4,5-diol	56.25	203	N/A	0.51
69	Anhydro-N-acetyl-glucosamine?	59.36	203	N/A	0.72
70	3-Acetamido-5-acetylfuran	60.71	167	95598-28-0	2.05
71	3-Acetamido-5-acetylfuran isomer	60.84	167	N/A	1.17
72	Unknown	61.42	181	N/A	0.10

Notes: Numbers in bold indicate the major pyrolysis constituents.  
Hydrogen, CO, methane, ethane, and water not included.

Similar to the case of glucose, it is expected that N-acetylglucosamine pyrolysate contains a number of compounds with multiple OH groups, and some of these compounds may not elute from the chromatographic column when conditions given in Table 4.6.1 are used. For this reason, a second experiment was performed by pyrolyzing 1.0 mg N-acetyl- $\beta$ -glucosamine at 900 °C followed by the collection of the pyrolysate and derivatization with BSTFA in conditions described in Section 4.6. The analysis of the derivatized pyrolysate was done using GC/MS technique in conditions described in Table 4.6.2. Only the window between 42 min and 52 min from the chromatogram of the derivatized pyrolysate

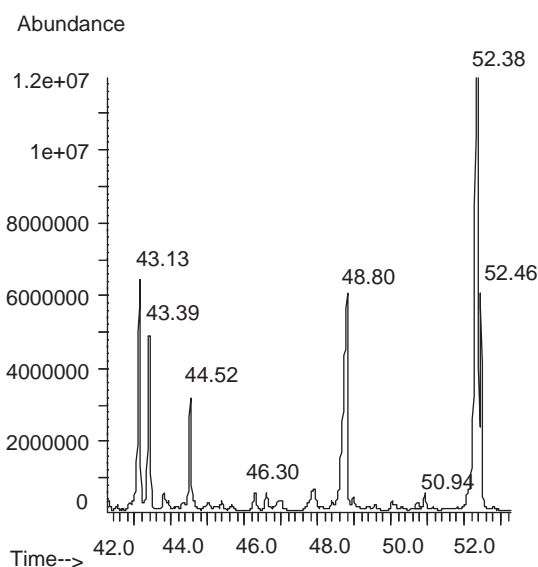


FIGURE 16.3.11. Time window of 42–52 min in the chromatogram of silylated *N*-acetylglucosamine pyrolysate.

TABLE 16.3.7. Identification of the main peaks in the time window 42–52 min in the chromatogram shown in Figure 16.3.11 for the pyrolysate of *N*-acetylglucosamine derivatized to TMS derivative with BSTFA

No.	Compound	Ret. time	No. of TMS	MW
1	2-(Acetylamino)-3,6-anhydro-2-deoxy-D-glucopyranose	43.13	2	347
2	6-(Hydroxymethyl)-2-methyl-4,5,6-trihydrocyclopenta[2,1-d]1,3-oxazole-4,5-diol	43.40	3	401
3	6-(Hydroxymethyl)-2-methyl-4,5,6,7,3a,7a-hexahydro-7-oxabenzoxazole-4,5-diol	44.52	3	419
4	Unknown	46.30	3	?
5	N-(3,4-Dihydroxy-7,8-dioxabicyclo[3.2.1]oct-2-yl)acetamide	48.80	2	347
6	N-Acetyl-2-deoxy-2-aminoglucose	52.38	4	509
7	N-Acetyl-2-deoxy-2-aminohexose	52.46	4	509

is shown in Figure 16.3.11, since this portion contains compound with OH silylated groups. The identification of the peaks is given in Table 16.3.7, based on their retention times.

The identification of silylated pyrolysis products of *N*-acetylglucosamine encountered problems due to the absence on their spectra in common mass spectral libraries. The mass spectra of 3 TMS 6-(hydroxymethyl)-2-methyl-4,5,6-trihydrocyclopenta[2,1-d]1,3-oxazole-4,5-diol is shown in Figure 16.3.12, 3 TMS derivative of 6-(hydroxymethyl)-2-methyl-4,5,6,7,3a,7a-hexahydro-7-oxabenzoxazole-4,5-diol is shown in Figure 16.3.13, and 2 TMS derivative of N-(3,4-dihydroxy-7,8-dioxabicyclo[3.2.1]oct-2-yl)acetamide, which is the equivalent of 2 TMS levoglucosan generated from glucose is shown in Figure 16.3.14.

As shown in Table 16.3.7, some of the initial compound is transferred unmodified by pyrolysis, and also some isomerization process takes place. The other compounds are generated from water elimination of one or more OH groups of the parent compound, in reactions either similar to that seen for simple sugars or as shown in reaction 16.3.7.

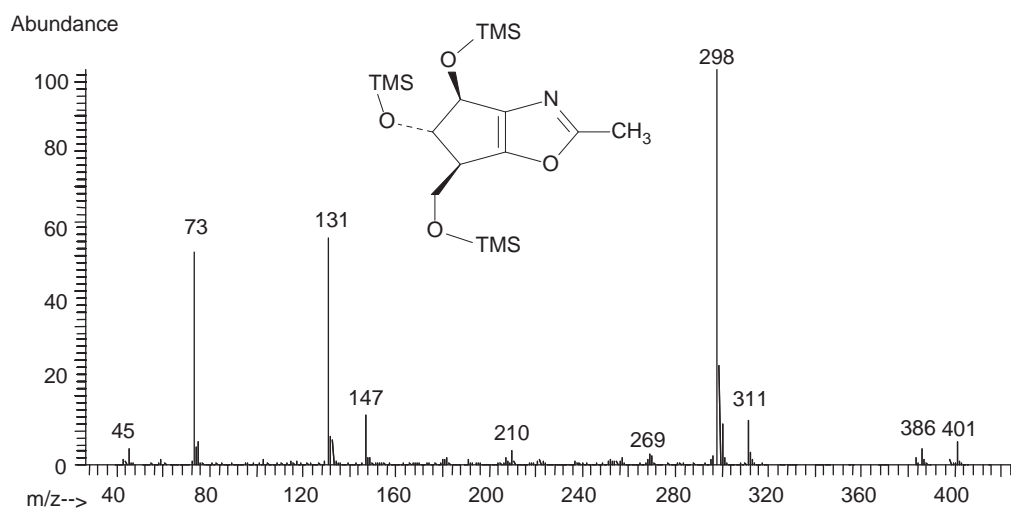


FIGURE 16.3.12. Mass spectrum of 3 TMS derivative of 6-(hydroxymethyl)-2-methyl-4,5,6-trihydro-cyclopenta[2,1-d]1,3-oxazole-4,5-diol (MW = 401).

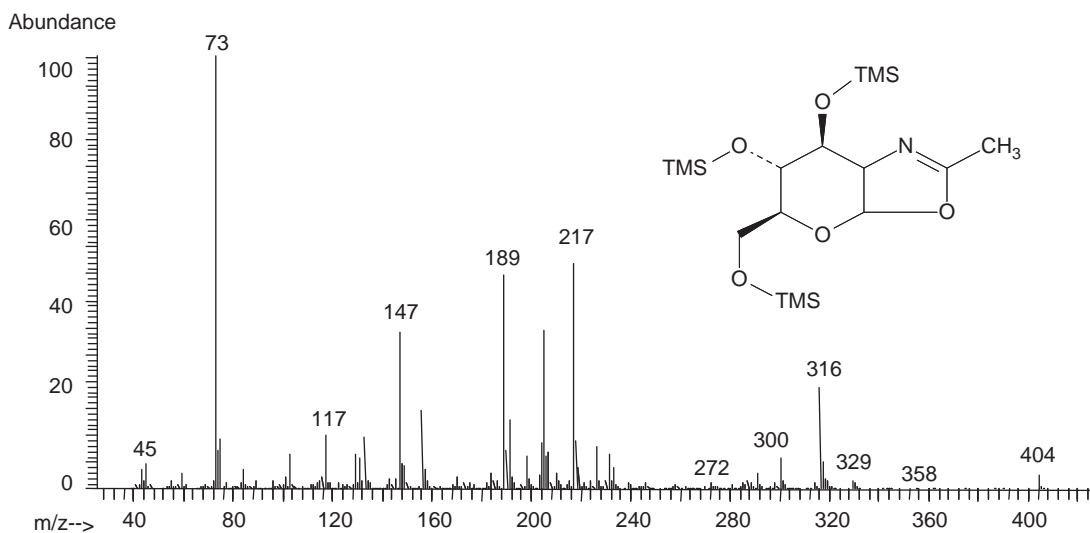


FIGURE 16.3.13. Mass spectrum of 3 TMS derivative of 6-(hydroxymethyl)-2-methyl-4,5,6,7,3a,7a-hexahydro-7-oxabenzoxazole-4,5-diol (MW = 419).

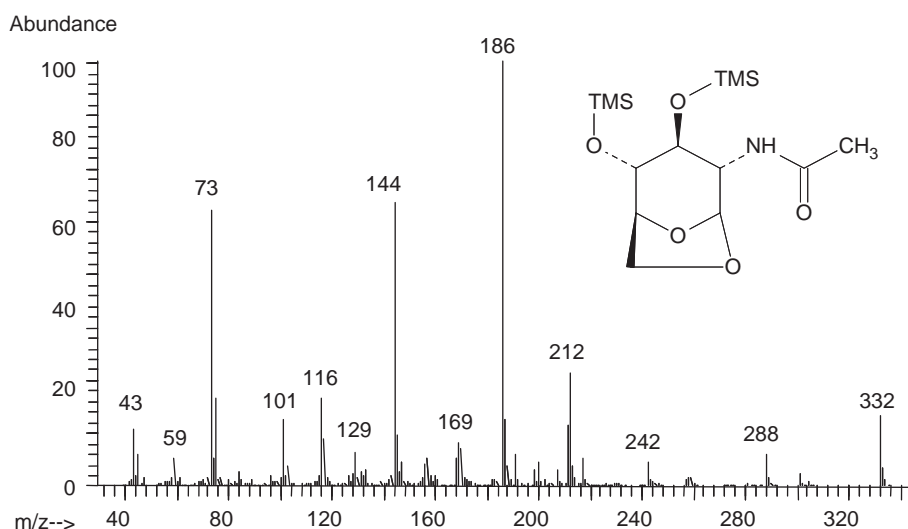


FIGURE 16.3.14. Mass spectrum of 2 TMS derivative of *N*-(3,4-dihydroxy-7,8-dioxabicyclo[3.2.1]oct-2-yl)acetamide (MW = 347).

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## CHAPTER 17

*Pyrolysis of Carboxylic Acids***17.1. MONOCARBOXYLIC ACIDS****General aspects**

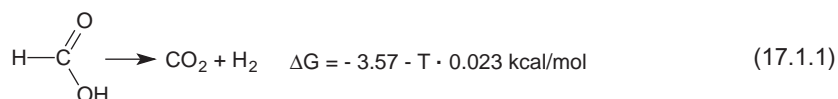
Carboxylic acids are characterized by the presence in their structure of one or more carboxyl groups ( $-\text{COOH}$ ), which bring to the molecule a proton donor character (acidic character). Carboxylic acids have the capability to form anions and salts (carboxylates). The carboxyl group can be connected to a simple aliphatic or aromatic radical R, as well as to heterocycles. Two types of names are used for organic acids. One is the common name ending with the suffix *ic* followed by *acid*, such as in formic acid, acetic acid, etc. The other is the IUPAC name. For simple acids, the IUPAC name starts with the name of the hydrocarbon with the same number of carbons as the acid replacing the suffix *e* with *oic* followed by *acid*. In this nomenclature formic acid is methanoic acid, propionic acid is propanoic acid, etc. For acids with multiple carboxylic groups, some have common names (e.g., oxalic acid, succinic acid, etc.) Also, the name can be made not counting the carbons in the carboxyl group and adding to the compound name *di-*, *tri-carboxylic acid*, etc. (e.g., propane-1,3-dicarboxylic acid for 1,5-pentadienoic acid or glutaric acid).

More complex molecules containing carboxyl groups are also common. Among these are chlorinated acids, hydroxy acids, acids containing carbonyl groups, etc. An important group of acids is that containing acids with additional amino groups (one or more). Amino acids play a key role in nature being the building blocks of peptides and proteins. Except for the amino acids, which are presented separately in Chapter 18, most types of organic acids are discussed in this chapter.

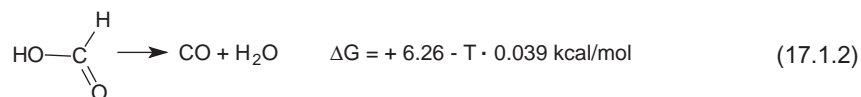
Both simple acids as well as complex acids are very common organic compounds, and their pyrolysis may occur in various processes.

**Formic acid**

A typical thermal decomposition of aliphatic monocarboxylic acids starts with their decarboxylation. However, this is not always the main or the only thermal decomposition process of acids. Formic acid  $\text{H}-\text{COOH}$ , which is the simplest carboxylic acid, can decompose by a unimolecular reaction as follows:



However, this acid has a special structure and can decompose by a reaction similar to that of aldehydes with water elimination:



At room temperature, the calculation of free enthalpy would show that reaction (17.1.1) is favored over reaction 17.1.2. However, the rate of formic acid decomposition at room temperature is



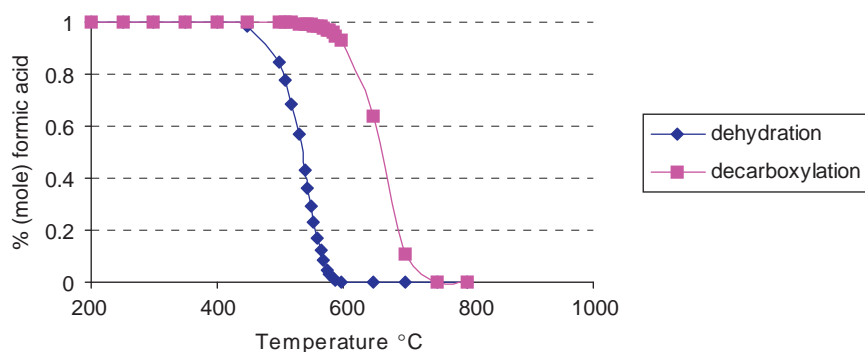


FIGURE 17.1.1. Calculation of the mole percent of formic acid at 0.01 s heating time as the temperature increases. The two processes were calculated as independent using the values for the decomposition rate constant for dehydration (rel. 17.1.4) and decarboxylation (rel. 17.1.3).

extremely low. At 300 °C both decomposition reactions have equal  $\Delta G$  values, and at higher temperatures the dehydration reaction is favored over decarboxylation [1]. Studies using shock wave experiments in the temperature range 1300–2000 K of formic acid diluted with Ar at a density of  $0.5\text{--}10^{-5}\text{--}2.5 \times 10^{-5} \text{ mol/cm}^3$  showed that the Arrhenius equation for the decarboxylation reaction 17.1.1 is given by the expression [2,3]:

$$k_{\text{decarb}} = 1.4 \times 10^{15} \exp \left[ \frac{-57 \text{ kcal/mol}}{RT} \right] \text{ cm}^3/\text{mol/s} \quad (17.1.3)$$

For the dehydration reaction 17.1.2 the Arrhenius equation has the expression:

$$k_{\text{dehyd}} = 2.3 \times 10^{15} \exp \left[ \frac{-50 \text{ kcal/mol}}{RT} \right] \text{ cm}^3/\text{mol/s} \quad (17.1.4)$$

The results of a calculation of formic acid decomposition for an exposure time of 0.01 s using these equations (as they would act independently) is shown in Figure 17.1.1.

Figure 17.1.1 illustrates the dominance of dehydration during formic acid pyrolysis. Experimental and theoretical studies showed that  $k_{\text{decarb}}/k_{\text{dehyd}} = 0.03\text{--}0.07$  and that formic acid thermal decomposition takes place mainly by dehydration process with the formation of CO, while the decarboxylation is only a minor process.

At lower temperatures, thermal decomposition of formic acid is also influenced by the formation of water or by the presence of water, which has a catalytic effect on formic acid pyrolysis [4,5]. Another detail regarding formic acid decomposition is related to the capability of this compound to form dimers. The dimers easily decompose as the temperature increases ( $k = 2 \times 10^4 \text{ s}^{-1}$  in the range 700–900 K) and do not affect the course of formic acid decomposition [3]. Several theoretical studies were performed on formic acid thermal decomposition [6,7].

### Acetic acid

At temperatures between 460 °C and 600 °C, acetic acid decomposes following two main reactions as shown below:

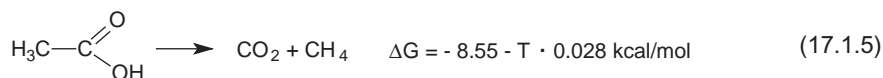
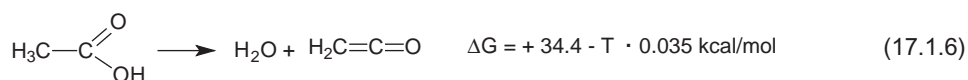
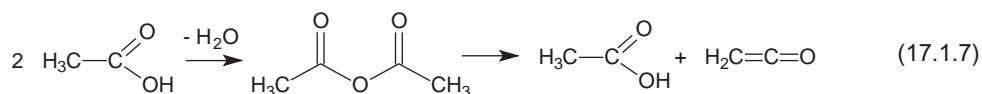


TABLE 17.1.1. Model reactions for acetic acid pyrolysis [10] and the corresponding Arrhenius parameters

Reaction	Log <sub>10</sub> A	E <sup>#</sup> (kcal/mol)	Type
CH <sub>3</sub> COOH → CH <sub>4</sub> + CO <sub>2</sub>	12.76	70.51	Overall kinetics
CH <sub>3</sub> COOH → CH <sub>2</sub> CO + H <sub>2</sub> O	12.72	70.51	Overall kinetics
CH <sub>2</sub> CO + M → CH <sub>2</sub> : + CO + M	15.76	61.66	Overall kinetics
CH <sub>2</sub> CO + CH <sub>2</sub> : → C <sub>2</sub> H <sub>4</sub> + CO	13.6	8.36	Overall kinetics
CH <sub>3</sub> COOH + CH <sub>2</sub> : → CH <sub>2</sub> :COOH + CH <sub>3</sub> ·	12	9.56	
CH <sub>2</sub> : + CH <sub>4</sub> → 2CH <sub>3</sub> ·	11.7	9.56	
CH <sub>3</sub> COOH + CH <sub>3</sub> · → CH <sub>2</sub> COOH + CH <sub>4</sub>	11.21	10.18	
CH <sub>3</sub> · + CH <sub>3</sub> · → C <sub>2</sub> H <sub>6</sub>	13	0	
CH <sub>3</sub> · + C <sub>2</sub> H <sub>6</sub> → C <sub>2</sub> H <sub>5</sub> · + CH <sub>4</sub>	11.78	11.59	



The formation of ketene can be attributed, at temperatures between 460 °C and 600 °C, to the formation of acetic anhydride from a bimolecular dehydration reaction and further decomposition of the anhydride to generate ketene and acetic acid [8,9]:



Ketene is prepared on industrial scale by this reaction at temperatures around 700 °C. Addition of ethyl phosphate as a catalyst increases the yield of ketene, and addition of a small amount of ammonia in the resulting gases diminishes the reverse reaction of ketene with H<sub>2</sub>O to form acetic acid.

Pyrolysis of acetic acid in the temperature range 1300–1950 K studied using shock wave experiments at 3–7 Torr of acetic acid partial pressure in dilution with argon [10] showed that both reactions 17.1.5 and 17.1.6 take place by a unimolecular mechanism. Although reaction 17.1.6 is endothermic at room temperatures, above 980 K the values for ΔG become negative and the reaction becomes favorable. Both reactions seem to have about equal rates between 1300 K and 1950 K. At temperatures above about 1600 K, the ketene intermediate decomposes very rapidly. The decomposition occurs both unimolecularly to methylene radicals and CO and also by radical reactions. Ethane is a minor product, and trace amounts of propene, propyne, and butenes are also observed at high temperatures. No products of chain length greater than C<sub>4</sub> were observed. Above 1700 K acetylene and hydrogen become major products with associated decreases in yields of methane, ethylene, and ethane.

A computer model for the decomposition kinetics of acetic acid involving 46 reactions of 21 species has been found to simulate well the experimental yield data. Sensitivity analyses have been used to identify reactions that make important contributions to the overall mechanism and yields of major products. Methylene radicals were found to play important roles in determining yields of major species. Some kinetic parameters used for this model are reported in the literature [10] and are given in Table 17.1.1.

Typical for unimolecular reactions, the kinetics depends on gas pressure and temperature. In the study conditions at 1300 K [10], reactions 17.1.5 and 17.1.6 are at high pressure limit, while at 1700 K they are in the falloff region with  $k/k^\infty = 0.82$ . Pyrolysis mechanism for acetic acid was also the subject of theoretical studies [11].

**Acetic acid homologs and substituted acetic acids**

Thermal decomposition of the homologs in the series of aliphatic monocarboxylic acids, such as propionic acid, butyric acid, 2-methylpropanoic acid (isobutyric acid), valeric acid, isovaleric acid (3-methylbutanoic acid), etc., takes place by reactions similar to those of acetic acid, following two main initial reactions: dehydration and decarboxylation. The dehydration reaction can be written as follows:



Depending on the temperature, heating time, and possible addition of catalysts, the hydrocarbon may continue the decomposition. The dehydration reaction of acids that would take place with the formation of a ketene is continued with the formation of CO and unsaturated hydrocarbons by the reaction:



The unsaturated hydrocarbons generated from the acid decomposition are mainly ethylene for propionic acid and a more complex mixture of unsaturated hydrocarbons for the other acids. The isolation of the individual ketenes is possible for some acids such as propionic acid, but it is not possible for other acids with larger molecules.

Thermal decomposition of longer chain acids, such as stearic, palmitic, myristic, or lauric, depends on temperature and heating time. At low temperatures between 250 °C and 300 °C and extended period of heating (3–4 h), the formation of ketenes was noticed. At higher temperatures, the formation of CO<sub>2</sub> and cleaving of the aliphatic chain is characteristic. Various hydrocarbon fragments and other compounds such as ketones and shorter chain carboxylic acids are seen in the pyrolysate. These fragments depend on the nature of the aliphatic radical R. For example, for a linear saturated aliphatic radical, the fragments are very similar to those of a linear saturated aliphatic hydrocarbon, and the main components are 1-alkenes, with the typical low levels of alkanes and alkadienes (see Chapter 7). Pyrolysis of oleic acid or (9Z)-octadec-9-enoic acid performed using flash pyrolysis to a  $T_{\text{eq}} = 750^\circ\text{C}$  for 15 s and analyzed by GC/MS generated the pyrogram in Figure 17.1.2 [12]. The separation was done on a 30 m HP5-MS column, which was held at an

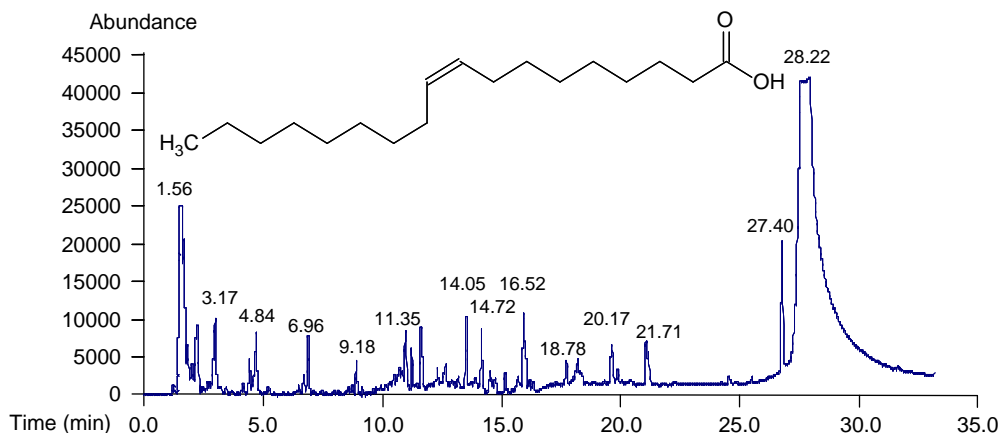


FIGURE 17.1.2. Pyrogram of oleic acid at 750 °C [12].

TABLE 17.1.2. Identification of the main peaks in the chromatograms shown in Figure 17.1.2 for the pyrolysis at 750 °C of oleic acid

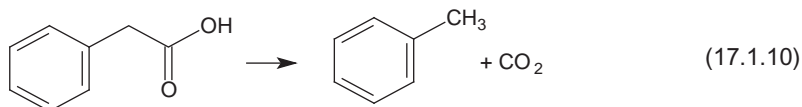
No.	Ret. time	Compound	No.	Ret. time	Compound
1	1.56	Carbon dioxide	33	12.78	Undeca-2 <i>E</i> ,4 <i>E</i> -diene
2	1.76	1,3-Butadiene	34	12.91	Cyclodecene
3	1.91	1-Pentene	35	13.14	Octanoic acid
4	2.08	1,3-Cyclopentadiene	36	13.38	1-Dodecene
5	2.14	Cyclopentene	37	13.68	Decanal
6	2.32	1-Hexene	38	14.05	5-Decyne
7	2.72	1,3,5-Hexatriene	39	14.24	1-Tertadecene
8	2.82	2,4-Hexadiene	40	14.72	( <i>E,Z</i> )-2,4-Dodecadiene
9	2.93	Benzene	41	14.86	Nonanoic acid
10	3.01	1,3-Cyclohexadiene	42	15.2	Cyclodecene
11	3.17	1-Heptene	43	15.28	1-Tridecene
12	3.72	Ethenylcyclopentane	44	15.81	( <i>E,E</i> )-1,4-Decadienal
13	3.95	1-Methylcyclohexene	45	15.92	5-Undecene
14	4.35	2-Methyl-1,3,5-hexatriene	46	16.52	1,12-Tridecadiene
15	4.43	Toluene	47	16.74	<i>n</i> -Decanoic acid
16	4.68	1,7-Octadiene	48	17.10	1-Tetradecene
17	4.84	1-Octene	49	18.46	1-Octylcyclohexene
18	5.47	Ethenylcyclohexane	48	18.53	( <i>Z,Z</i> )-1,6-Tridecadiene
19	5.54	1,3-Octadiene	49	18.79	1-Pentadecene
20	6.96	1-Nonene	50	19.43	1-Octadecyne
21	7.15	Cyclooctene	51	20.13	( <i>Z</i> )-Cyclododecene
22	7.72	1,1'-(1,2-Ethanediy)bis-cyclopropane	52	20.17	1-Hexadecyne
23	7.91	2-Cyclohexen-1-one	53	20.39	Cyclotetradecane
24	8.23	1-Butyl-cyclopentene	54	20.59	<i>cis</i> -7-Tetradecen-1-ol
25	8.87	5-Hexenoic acid	55	21.61	Decahydronaphthalene
26	9.18	1-Decene	56	21.71	( <i>E</i> ?) -8-Heptadecene
27	9.45	Octanal	57	21.78	( <i>Z</i> ?) -8-Heptadecene
28	10.83	1,3-Nonadiene	58	22.38	9-Octadecyne
29	11.24	Heptanoic acid	59	25.14	( <i>E</i> )-9-Octadecenoic acid
30	11.35	1-Undecene	60	26.12	( <i>Z</i> )-9-Octadecenal
31	11.82	4-Undecene	61	27.40	9-Octadecenoic acid methyl ester
32	12.05	1,3-Nonadiene	62	28.44	( <i>Z</i> )-9-Octadecenoic acid

initial temperature of 40 °C for 2 min, then ramped at 8 °C/min to a final temperature of 300 °C where it was held for 5 min. The peak identification done with mass library searches is given in Table 17.1.2.

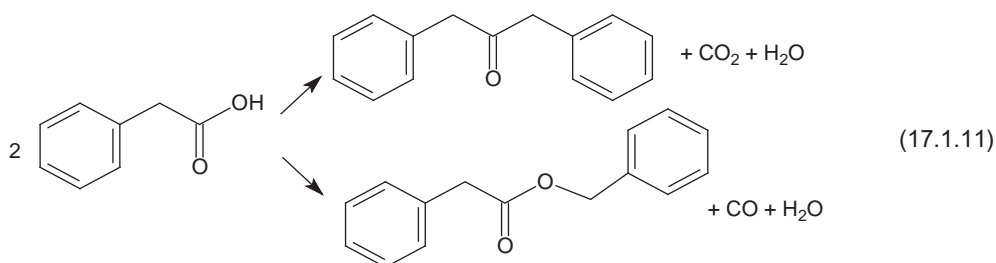
As shown in Table 17.1.2, the pyrogram of oleic acid is rather complex. A large part of the acid remains undecomposed. Besides 9-octadecenoic acid methyl ester, the alkenes and the alkadienes are the main peaks in the pyrogram.

A number of acids are derived from acetic acid by substituting one or more hydrogens from the CH<sub>3</sub> group with other substituents. A typical example is phenyl acetic acid. By pyrolysis around 600 °C, this

compound generates mainly toluene by a typical decarboxylation reaction:



In addition to toluene, some phenylacetic acid phenyl methyl ester and small levels of other compounds such as bibenzyl, and 1,3-diphenyl-2-propanone are formed. The reactions leading to 1,3-diphenyl-2-propanone and to phenylacetic acid phenyl methyl ester are shown below:

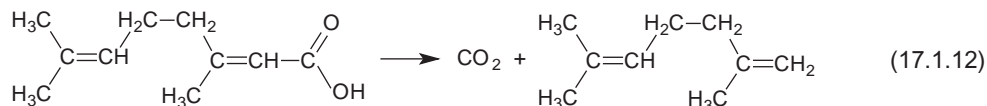


The acids generated by the substitution of all hydrogens from the  $\text{CH}_3$  fragment of acetic acid, have a stronger tendency to decarboxylate at lower temperatures compared to the other substituted acetic acids [13]. Also, when the substituent is alkyl, the stability of the acid is higher compared to the case of aromatic substituents. For example, the decomposition of 3-phenylpropionic acid takes place at higher temperatures than that of phenyl acetic acid, and the pyrolysate is more complex with lower levels of ethylbenzene compared to the level of toluene in the case of phenyl acetic acid.

The relatively easy to occur decarboxylation reaction of substituted acetic acids has been used for the synthesis of various compounds. Among the compounds that can be obtained by this procedure are *N*-methyl- $\alpha$ -pyridone from 2-pyridone-1-acetic acid and 3-(hydroxylamino)butan-2-one from 3-(hydroxylamino)-4-oxopentanoic acid. [13].

### Acids with $\alpha,\beta$ -unsaturation and with $\beta,\gamma$ -unsaturation

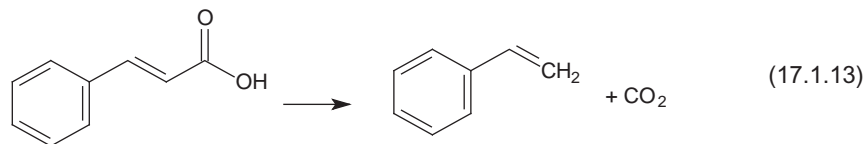
Acrylic acid is relatively stable to heating. Its pyrolysis generates  $\text{CO}_2$  and ethylene by a simple decarboxylation reaction, but also a number of other molecules, including aromatic compounds generated by various condensation processes. Other acids with  $\alpha,\beta$ -unsaturation also eliminate  $\text{CO}_2$  with more or fewer additional reactions, depending on the temperature and the nature of the acid. The decomposition at lower temperatures has the tendency to lead to decarboxylation as a unique reaction, while pyrolysis at higher temperatures generates a more complex pyrolysate. For example, geranic acid (3,7-dimethyl-2,6-octadienoic acid) at  $250^\circ\text{C}$  decomposes following the reaction:



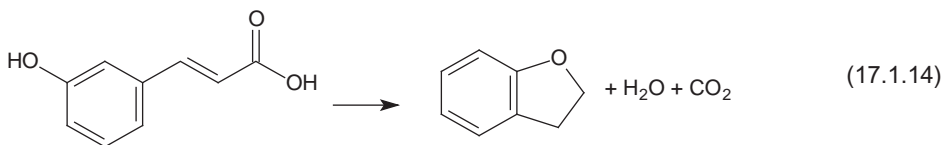
At higher temperatures a complex mixture including aromatic molecules is generated.

The substituent on the  $\beta$ -carbon to the carboxyl group plays an important role regarding the outcome of the pyrolytic process, as shown below for several substituted cinnamic acids. The main

decomposition reaction for cinnamic acid at 900 °C is the formation of styrene as shown below:

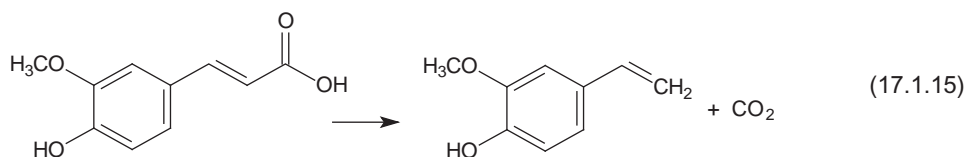


Pyrolysis of 3-hydroxycinnamic acid (3-coumaric acid) generates at 900 °C mainly 2,3-dihydrobenzofuran, which shows that the substitution on the benzene ring has a major influence on the pyrolysis outcome:

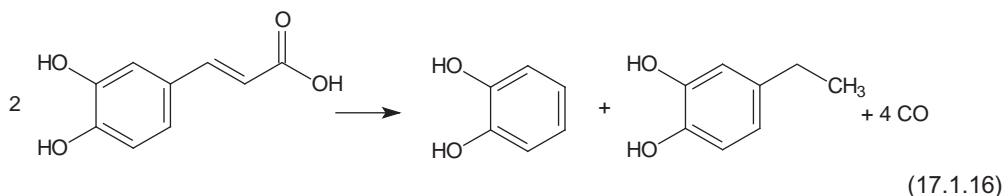


Levels around 2–3% of 3-methylphenol, 2H-1-benzopyran-2-one, and 7-hydroxy-1-indanone are also generated in the pyrolysate.

Ferulic acid (4-hydroxy-3-methoxycinnamic acid) at 900 °C generates as a main pyrolysis product 2-methoxy-4-vinylphenol in a reaction similar to that of cinnamic acid. This result is different from that for 3-coumaric acid and indicates that some substitutions on the benzene ring do not influence the pyrolysis outcome:



Caffeic acid (4,3-dihydroxycinnamic acid) decomposes differently from the other substituted cinnamic acids, leading to CO<sub>2</sub>, CO, and about equal proportions at around 30% (molar) of catechol and 4-ethylcatechol:

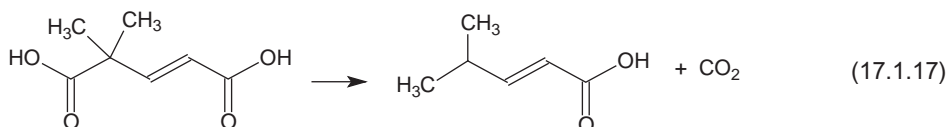


Another pyrolysis product of caffeic acid at about 8% (molar) is 3-(3,4-dihydroxyphenyl)prop-2-enal. Small levels of phenol, methyl, and ethylphenol were also present in caffeic acid pyrolysate.

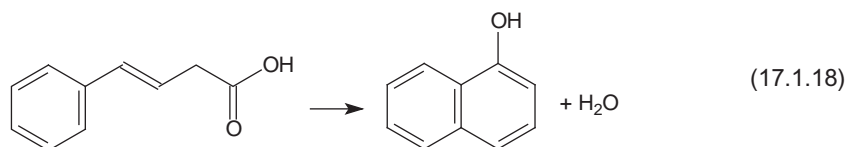
The main pyrolytic route seen for cinnamic acid and for ferulic acid not being the same either for 3-coumaric acid or for caffeic acid shows the importance of the rest of the molecule in the type of reactions taking place during pyrolysis.

Decarboxylation is also typical for  $\beta,\gamma$ -unsaturated acids. Among the compounds with the pyrolysis process reported in the literature [13] is, for example, 3,3-dimethylprop-1-ene-1,3-dicarboxylic acid,

which eliminates CO<sub>2</sub> around 200 °C, affecting only the carboxyl in 3-position:



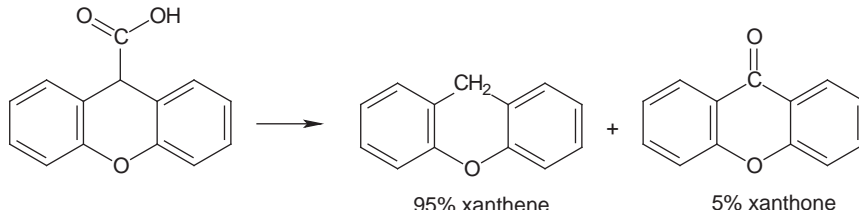
In contrast, 4-phenyl-3-butenic acid (phenylisocrotonic acid) generates  $\alpha$ -naphthol by eliminating water during pyrolysis [14]:



The formation of stable aromatic compounds influences the reaction path of reaction 17.1.18. Comparing reactions 17.1.17 and 17.1.18, it can be seen that in one case pyrolysis occurs with CO<sub>2</sub> elimination, and in the second case with H<sub>2</sub>O elimination, the difference being caused by the high stability of  $\alpha$ -naphthol.

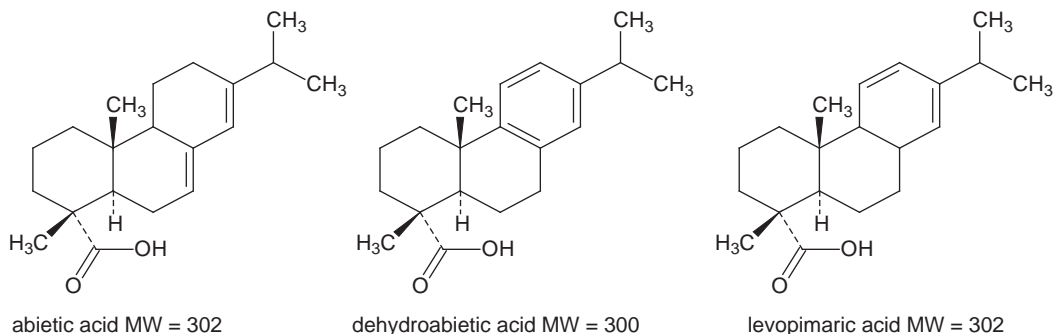
### Other aliphatic acids

There are numerous acids present in nature or generated synthetically. Their pyrolysis can take place with CO, CO<sub>2</sub>, and/or H<sub>2</sub>O formation, but the outcome of the thermal decomposition also depends on the molecular structure of the parent compound correlated to the stability at elevated temperatures of the potential pyrolysis products. For example, xanthene-9-carboxylic acid decomposes as shown below:



The formation of xanthene takes place by decarboxylation, while the low level of xanthone should be the result of CH<sub>2</sub>O formation, but formaldehyde (even in traces) is not detected in the pyrolysate.

More complex molecules can undergo, in parallel with the decarboxylation, other reactions that will modify the expected outcome. Among the acids with more complex structures are those found in coniferous resin. The acids are present there together with several terpenes, which can be vaporized to leave a solid material known as rosin. Among the main acids in rosin are abietic acid, neoabietic acid, dehydroabietic acid, palustric acid, and levopimaric acid. The structures of abietic acid, dehydroabietic acid, and levopimaric acid are shown below:



Pyrolysis of acids from rosin has been of interest for the potential formation of precursors that can be used in the synthesis of steroids [15]. Also, pyrolysis of rosin acids is related to analytical techniques applied to various cultural materials (rosin was used in old varnishes) [16,17], identification of authentic amber [18], characterization of resins [19,20], etc. Regarding environmental issues, pyrolysis of rosin core solder was evaluated for potential generation of aldehydes [21]. Pyrolysis between 400 °C and 500 °C of abietic, dehydroabietic, and levopimaric acids has been reported in the literature [15,22]. Pyrolysis of a sample of abietic acid performed on 1.0 mg compound in a Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900\text{ °C}$ ,  $\beta = 10\text{ °C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280\text{ °C}$ , generates  $\text{CO}_2$  and low levels of several small molecules including methanol, acetaldehyde, and acetone. Traces of various alkyl substituted cyclopentanes, cyclopentenenes, cyclohexanes, cyclohexenes, cyclohexadienes, benzenes, and naphthalenes were detected in the pyrolysate. These include 3,5-dimethylcyclopentene, 1,3-dimethylcyclohexene, 3,3,5-trimethylcyclohexene, 1,2-dimethyl-1,4-cyclohexadiene, toluene, xylenes, 1-ethyl-2-methylbenzene, 1-methyl-3-isopropylbenzene, 1-ethyl-4-isopropylbenzene, 2,3-dihydro-2,2-dimethyl-1H-indene, 3-(1,1-dimethyl)-1,2-dihydronaphthalene, and 1-methyl-7-isopropyl-naphthalene. All these molecules were obviously generated from the fragmentation and dehydrogenation of the decahydrophenanthrene ring system. The main pyrolysis products were molecules showing less fragmentation. Their separation was obtained using GC conditions as described in Table 4.6.2. These conditions involved a less polar chromatographic column and higher temperatures for the elution of pyrolysate constituents. The time window between 47 min and 63 min in the pyrogram is shown in Figure 17.1.3. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 17.1.3. The calculation of the mole percent was obtained based on peak areas.

As shown in Table 7.1.3, about 43% of the abietic acid is not decomposed in the experimental conditions selected for pyrolysis. The presence of about 9% of dehydroabietic acid in the pyrolysate indicates that dehydrogenation is an important reaction during abietic acid pyrolysis. It is possible that decarboxylation is also the first step in the formation of 4*b*,8-dimethyl-2-isopropyloctahydrophenanthrene (and isomers), where both decarboxylation and dehydrogenation occurred. It is reasonable to consider the main reactions in abietic acid pyrolysis as

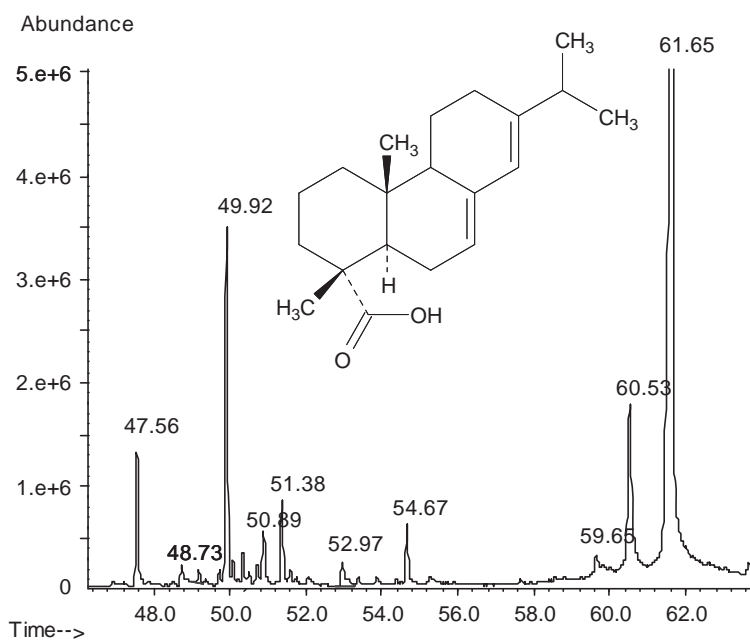


FIGURE 17.1.3. Time window 47–63 min in the pyrogram of 1.0 mg abietic acid at 900 °C.

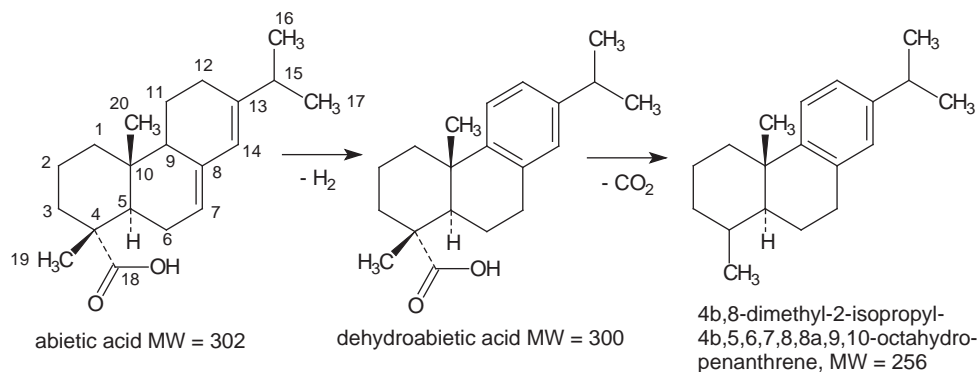


TABLE 17.1.3. Identification of the main peaks in the pyrogram of abietic acid at 900 °C (hydrogen, CO, methane, ethane, and water not included)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide (not shown in Figure 17.1.3)	4.17	44	124-38-9	<b>10.13</b>
2	Acetone (not shown in Figure 17.1.3)	8.96	58	67-64-1	6.59
3	Other (not shown in Figure 17.1.3)	Various	Average 130	N/A	2.73
4	4b,8-Dimethyl-2-isopropyl-4b,5,6,7,8,8a,9,10-Octahydrophenanthrene (isomer)	47.56	256	N/A	3.93
5	Norabieta-3,8,11,13-tetraene isomer	48.73	254	N/A	0.75
6	1-Methyl-7-isopropyl-decahydrophenanthrene	49.19	258	N/A	0.36
7	19-Norabieta-4(18),8,11,13-tetraene	49.74	254	N/A	0.46
8	4b,8-Dimethyl-2-isopropyl-4b,5,6,7,8,8a,9,10-octahydrophenanthrene (19-norabieta-8,11,13-triene)	49.92	256	N/A	<b>10.45</b>
9	4b,8-Dimethyl-2-isopropyl-4b,5,6,7,8,8a,9,10-octahydrophenanthrene (isomer)	50.09	256	N/A	0.75
10	4b,8-Dimethyl-2-isopropyl-4b,5,6,7,8,8a,9,10-Octahydrophenanthrene (isomer)	50.34	256	N/A	0.98
11	Norabieta-3,8,11,13-tetraene isomer	50.73	254	N/A	0.73
12	1,4a-Dimethyl-7-isopropyl-tetrahydrophenanthrene	50.90	252	N/A	2.06
13	19-Norabieta-4,8,11,13-tetraene	51.38	254	N/A	<b>2.52</b>
14	Unknown isomer	51.59	256	N/A	0.38
15	4,4'-Diisopropylbiphenyl?	52.97	238	18970-3-4	1.21
16	Norabieta-3,8,11,13-tetraene	54.67	254	N/A	1.88
17	Palustric acid (impurity in abietic acid)	59.65	302	1945-53-5	1.19
18	Pimaric acid (impurity in abietic acid)	59.82	302	127-27-5	0.55
19	Dehydroabietic acid	60.53	300	1740-19-8	<b>9.07</b>
20	Abietic acid	61.65	302	514-10-3	<b>42.89</b>
21	Dehydroabietic acid isomer	63.67	300	N/A	0.37

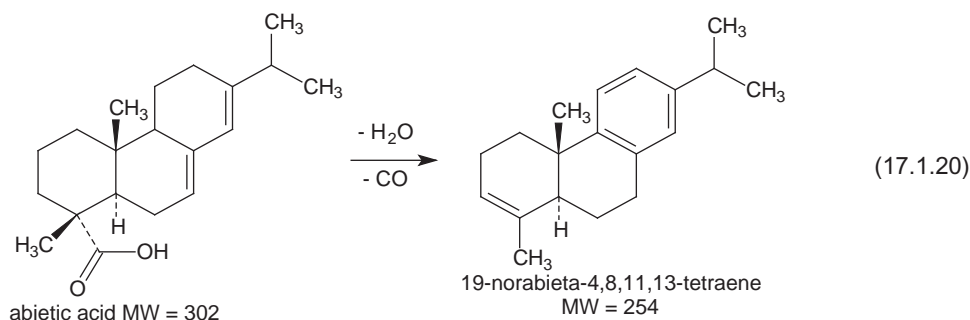
Note: Numbers in bold indicate the major pyrolysis constituents.

being the following:



(17.1.19)

Elimination of CO and water from dehydroabietic acid also explains the formation of norabietate-traenes (MW = 254) in the pyrolysate.



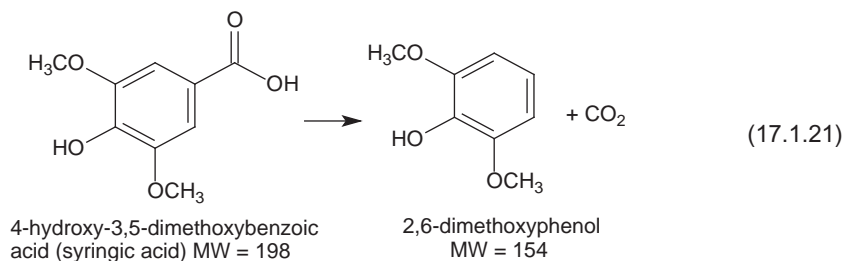
Several other terpene-related acids are found in plants and animals. Some of them have, besides carboxyl, other groups including OH, carbonyl, etc. Among many examples containing OH groups are bile acids (cholic acid, deoxycholic acid) and boswellic acid (which contains a pentacyclic triterpene molecule). Keto- $\beta$ -boswellic acid and glycyrrhetic acid contain both OH and a carbonyl group. Pyrolysis of these molecules typically takes place with decarboxylation as an initial step followed by further decomposition similar to that of sterols (see Section 9.1).

### Aromatic monocarboxylic acids

Benzoic acid decomposes around 500 °C with the formation of benzene and CO<sub>2</sub>, following a typical decarboxylation reaction. At higher temperatures, a more complex mixture of compounds is generated, including biphenyl, *p*-phenylbenzoic acid, and traces of benzaldehyde and 4,4'-dicarboxybiphenyl.  $\alpha$ -Naphthoic acid behaves similarly to benzoic acid. The formation of naphthyl-naphthalene was also detected in the pyrolysate of  $\alpha$ -naphthoic acid.

Online pyrolytic methylation of benzoic acid has been successfully used for the analysis of this compound as its methyl ester. The analysis used tetramethylammonium hydroxide (TMAH) as a methylating reagent. The pyrolytic methylation was performed directly in the injection port of a GC system at 280 °C and was applied for the analysis of benzoic acid in soft drinks [23].

Due to the high stability of the aromatic rings at elevated temperatures, many other aromatic acids decompose at elevated temperatures by the decarboxylation reactions. For example, gallic acid (3,4,5-trihydroxybenzoic acid) pyrolyzed at 900 °C in flash pyrolysis conditions generates mainly 3,4,5-trihydroxybenzene and traces of dihydroxybenzenes [24]. Syringic acid (4-hydroxy-2,3-dimethoxybenzoic acid) pyrolyzed at 900 °C in flash pyrolysis conditions generates mainly 2,6-dimethoxyphenol [24]. Only 3-methoxy-1,2-benzenediol and 3,4,5-trimethoxybenzoic acid were found at levels around 4–5% in the pyrolysate, while other aromatic compounds such as dihydroxybenzenes, methoxyhydroxybenzenes, methoxymethyl-phenol, etc. were present at trace levels. The main reaction of thermal decomposition of syringic acid is shown below:



A comparison of the decomposition of syringic acid with that of syringaldehyde (see Section 15.1) shows that a large portion of syringaldehyde remains undecomposed by flash pyrolysis at 900 °C, while syringic acid is completely decomposed in these conditions. Syringaldehyde generates more low levels of various fragments compared to syringic acid.

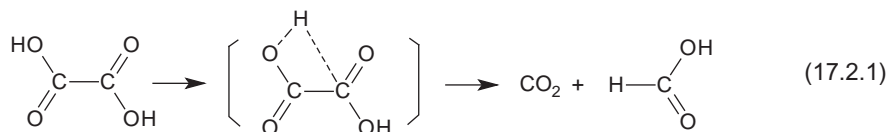
## 17.2. DI- AND POLYCARBOXYLIC ACIDS

### General aspects

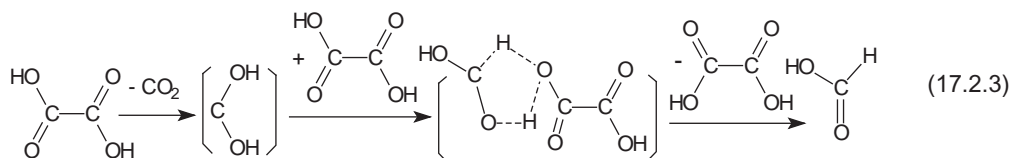
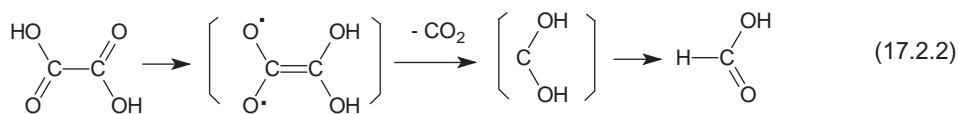
Thermal decomposition of organic acids with two or more COOH groups in the molecule may take place at a single carboxyl group or with simultaneous participation in the decomposition process of both groups. This behavior is mainly determined by the structure of the acid, particularly by the relative position of the COOH groups in the acid molecule. Dibasic acids, in particular, are common compounds with numerous applications in practice, and their pyrolysis may take place in various instances.

### Oxalic acid

Thermal decomposition of dry oxalic acid (oxalic acid is also common as a dihydrate) starts at relatively low temperatures, around 140 °C. In water solution, the decomposition starts even at lower temperatures. The main decomposition products are H<sub>2</sub>O, CO, and CO<sub>2</sub>. This decomposition has been evaluated experimentally at different temperatures [25–27] as well as theoretically [28]. Experimental results regarding the decomposition of oxalic acid in the range 400–430 K showed that the first stage of decomposition leads to formic acid and CO<sub>2</sub>. One of the mechanisms suggested for this reaction is shown below:

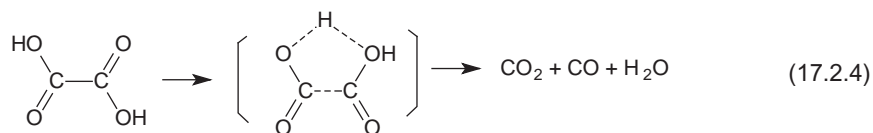


Upon further heating, the formic acid from reaction 17.2.1 is decomposed into CO and H<sub>2</sub>O as previously shown (see Section 17.1). Regarding the mechanism of reaction 17.2.1, it can be argued that the migration of a hydrogen atom to a carbon requires a relatively high energy (of about 67.4 kcal/mol) and that other mechanisms should be possible. The formation of dihydroxylcarbene as an intermediate species is one of these potential mechanisms [29]. A dihydroxylcarbene can be generated from oxalic acid by decarboxylation, following one of the two paths shown as follows:



The mechanism of reaction 17.2.2 is unimolecular, and reaction 17.2.3 is bimolecular.

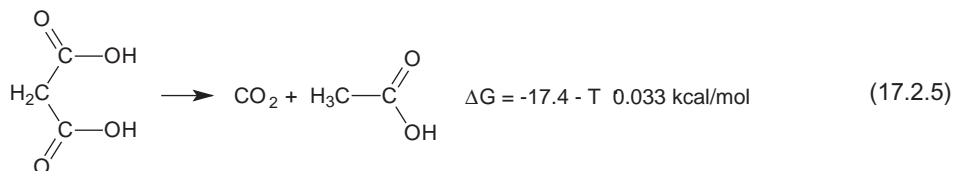
Another mechanism of oxalic acid decomposition, which does not involve the formation of formic acid (although this was detected in the pyrolysis process), is shown below:



Theoretical calculations [28] predicted that unimolecular formation of carbon dioxide and dihydroxylcarbene from oxalic acid is a feasible thermal process, but unimolecular formation of HCOOH from dihydroxylcarbene (reaction 17.2.2) has an activation barrier that is higher than unimolecular formation of CO<sub>2</sub>, CO, and H<sub>2</sub>O from oxalic acid via a concerted transition state (reaction 17.2.4). In contrast, hydrogen migration from oxygen to carbon of dihydroxylcarbene to produce HCOOH can be accomplished through a hydrogen exchange with another molecule of oxalic acid (or with a water molecule) in a bimolecular process with an activation barrier lower than all unimolecular decomposition channels considered. This indicates that at lower temperature the preferred decomposition mechanism may follow reaction 17.2.3. Transition state theory calculations indicate that this bimolecular channel might be responsible for the rapid formation of CO<sub>2</sub> and HCOOH in gas phase oxalic acid decomposition. With increasing temperature the unimolecular channel to produce CO<sub>2</sub>, CO, and H<sub>2</sub>O by reaction 17.2.4 might become significant.

### Malonic and malonic type acids

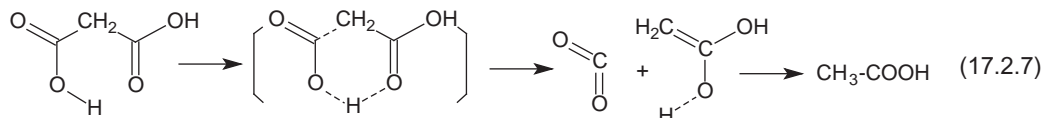
Malonic acid (methane-1,1-dicarboxylic acid) loses CO<sub>2</sub> starting around 140 °C to generate acetic acid by the following reaction:



Minor compounds in the pyrolysate are CO (5%), acetone (3%), C<sub>2</sub>H<sub>6</sub> (0.4%), and CH<sub>4</sub> (0.2%), all relative to CO<sub>2</sub> at 92 °C. The formation of CO<sub>2</sub> follows a first-order kinetics for conversions up to 50% and in the pressure range 0.12–0.7 Torr. The Arrhenius equation for the reaction in gas phase has the expression [30]:

$$k = 10^{13.27} \exp \left[ \frac{-30.9 \text{ kcal/mol}}{RT} \right] \text{ s}^{-1} \quad (17.2.6)$$

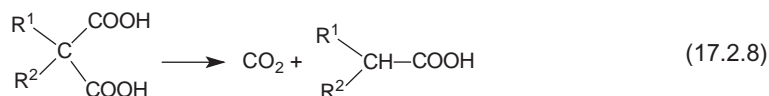
Similar to the case of oxalic acid, the decomposition of malonic acid in water solution starts at a lower temperature (about 70 °C). The decomposition mechanism of malonic acid is probably similar to that of oxalic acid, as shown in the following reaction:



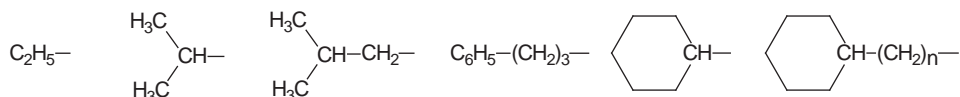
The formation of an ethene-1,1-diol as an intermediate species is not unlikely, since 2,2-substituted ethene-1,1-diols are known substances that easily isomerize into acids (see, e.g., [31]). Thermal

decomposition of malonic acid in molten form was studied above the melting point of the compound, as well as below the melting point when malonic acid can exist as a supercooled liquid. Some differences in the reaction kinetics were found between gas phase and the two forms of melted malonic acid [32].

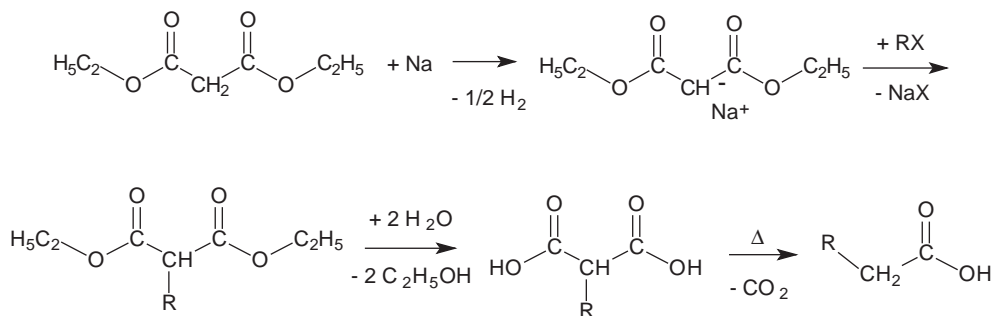
The “clean” decarboxylation at a relatively low temperature of malonic acid is also characteristic for a number of substituted malonic acids with the general formula  $R-CH(COOH)_2$ , and  $R_2C(COOH)_2$ . The decarboxylation reaction for these acids can be written as follows:



Both  $R^1$  and  $R^2$  in reaction 17.2.8 can be H, or one of them can be H and other possible substituents are shown below:

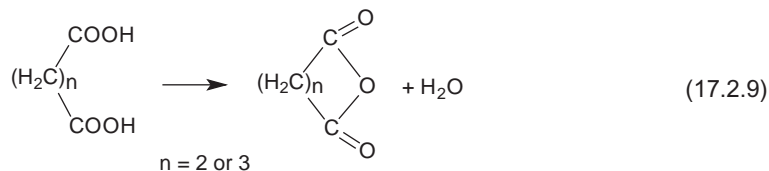


Many other examples of malonic acids substituted at the  $CH_2$  group decomposing by reaction 17.2.8 are indicated in the literature [13]. Reaction 17.2.8 provides an efficient path to synthesize organic acids with the formula  $R-CH_2-COOH$  from a halogenated compound  $R-X$ . The reactions typically starts with diethyl malonate in the following chain of reactions:

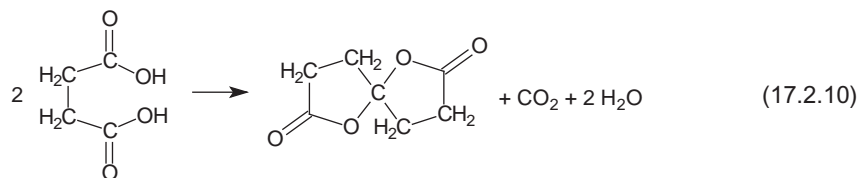


### Succinic and glutaric type acids

The main reaction during thermal decomposition of succinic acid,  $HOOC-(CH_2)_2-COOH$  (butanedioic acid), and glutaric acid,  $HOOC-(CH_2)_3-COOH$  (pentanedioic acid), is the formation of anhydrides by elimination of water. Succinic acid starts decomposing around 200 °C and glutaric acid around 300 °C [33]. The reaction leads to the formation of anhydrides and can be written as follows:

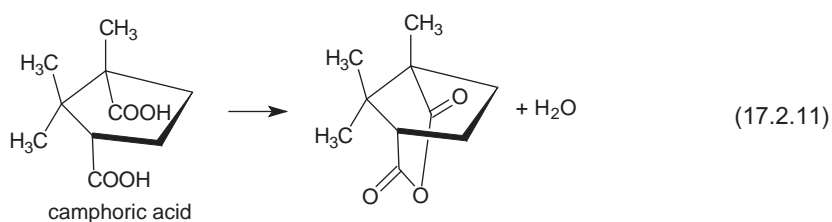


By prolonged heating around 250 °C the anhydride or a mixture of the acid and the anhydride will generate 1,6-dioxaspiro[4.4]2,7-dione by the following reaction:

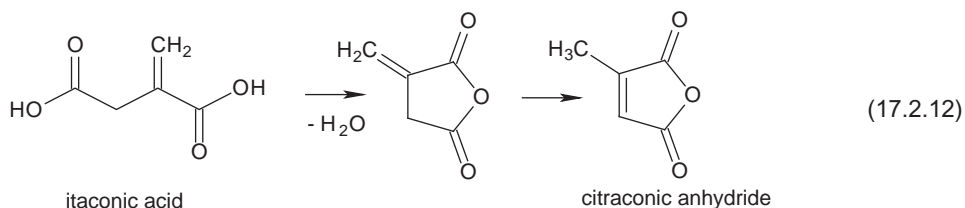


Substituted succinic acids also form anhydrides and eliminate  $\text{H}_2\text{O}$  when they are pyrolyzed. This has been reported in the literature [34] for methyl-, ethyl-,  $\alpha,\alpha$ -dimethyl-,  $\alpha,\beta$ -dimethyl-, and other substituted succinic acids. The formation of anhydrides and  $\text{H}_2\text{O}$  elimination is the first process for many other acids that contain the  $\text{HOOC}-\text{C}-\text{C}-\text{COOH}$  structure in their molecule.

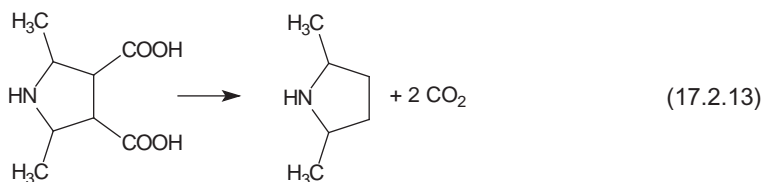
The same process of water elimination has been reported for glutaric acid. This compound eliminates water with the formation of an anhydride starting at temperatures around  $250\text{--}300^\circ\text{C}$ . The anhydride is stable and remains the main pyrolysis product at higher temperatures. Various other compounds containing the  $\text{COOH}$  groups on a three-carbon aliphatic chain easily form anhydrides. This includes acids with aliphatic or aromatic groups substituted on the carbon chain, acids with the three carbons involved in a saturated cycle such as 2-(carboxymethyl)cyclohexane carboxylic acid [13], etc. The formation of an anhydride is shown below for camphoric acid, which also contains the same carbon chain as glutaric acid.



The involvement in a double bond of one of the carbon atoms from the chain connecting the carboxyl groups does not seem to affect the formation of anhydrides. This can be seen, for example, in the formation of an anhydride at a relatively low temperature for 2-methylenesuccinic acid (itaconic acid). The resulting anhydride easily suffers a migration of the double bond to generate citraconic anhydride:



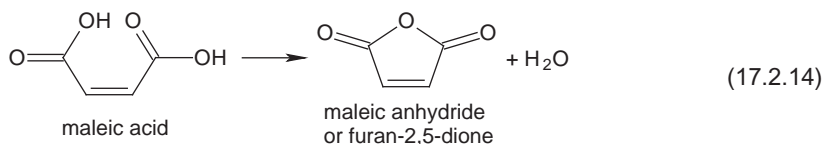
The reaction of water elimination with the formation of anhydrides, although typical for acids with succinic or glutaric type structures, is not always followed for the acids with similar local structure if the rest of the molecule imposes other reactions. For example, 3,5-dimethylpyrrolidine-3,4-dicarboxylic acid does not form an anhydride upon heating above  $250^\circ\text{C}$ , but eliminates  $\text{CO}_2$  following the reaction:



The same behavior, of not forming an anhydride is seen for other dicarboxylic acids with the two  $\text{COOH}$  groups attached to  $\alpha$ - or  $\beta$ -carbons that are part of a heterocycle (see Section 17.4).

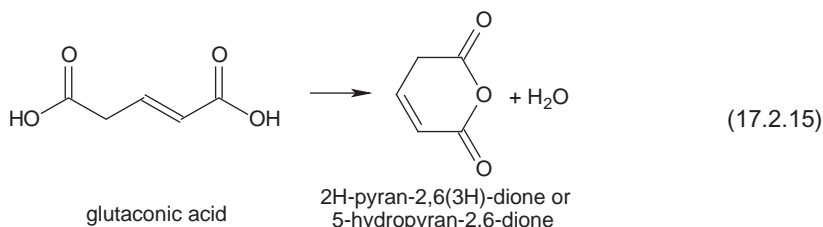
**Maleic, fumaric, and glutaric acids**

The presence of a double bond included in the chain connecting the two carboxyl groups, as present in maleic, fumaric, and glutaric acids, does not preclude the formation of anhydrides from the acids upon heating. Maleic acid, also known as (*Z*)-butenedioic or *cis*-butenedioic, starts losing water around 160 °C, generating maleic anhydride. Maleic anhydride is stable at elevated temperatures, and it is the main pyrolysis product of maleic acid. The reaction is shown below:

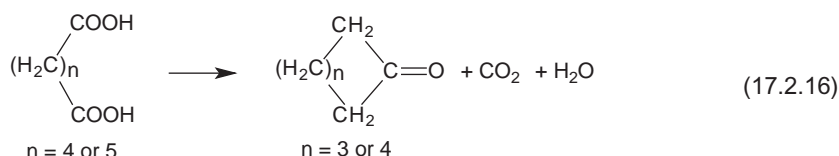


Fumaric acid or (*E*)-butenedioic acid also generates maleic anhydride, but some decarboxylation and char formation is noted upon heating.

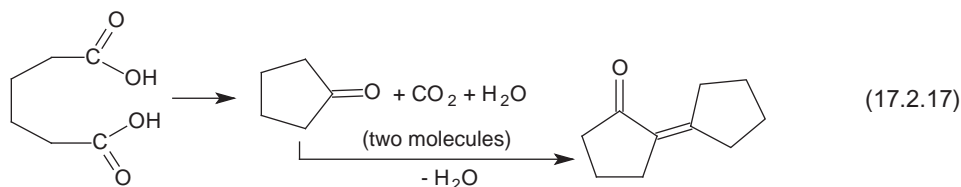
Glutaric acid has a *cis* and a *trans* form due to the presence of the double bond. Similarly to maleic and fumaric acids, glutaric acid generates by pyrolysis 2H-pyran-2,6(3H)-dione.

**Adipic and pimelic type acids**

Adipic acid (hexanedioic acid) and pimelic acid (heptanedioic acid) pyrolyze differently from the acids with a smaller number of carbon atoms. The typical reaction for these acids is the elimination of H<sub>2</sub>O and CO<sub>2</sub> with the formation of a ketone by the following reaction:



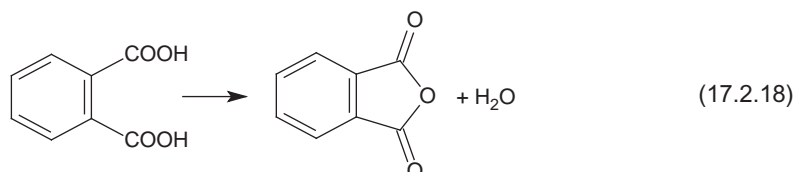
The decomposing of the acids starts around 350–400 °C, but the reaction has the same result even at higher temperatures. Pyrolysis of adipic acid at 900 °C in a flash pyrolysis experiment generated mainly cyclopentanone and some undecomposed adipic acid [24]. Low levels of 2-cyclopentylidenecyclopentan-2-one were also found in the pyrolysate. The reactions leading to cyclopentanone and further to 2-cyclopentylidenecyclopentan-2-one are shown below:



Substituted adipic and pimelic acids can be used for the preparation of ketones using reactions of the type 17.2.16.

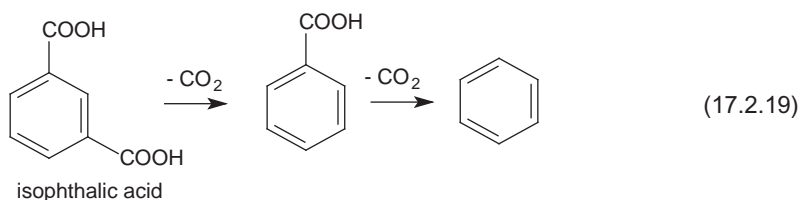
### Aromatic dicarboxylic acids

Phthalic acids (1,2-, 1,3-, and 1,4-benzenedicarboxylic acids) are the simplest aromatic dicarboxylic acids. Thermal decomposition of *o*-phthalic acid (1,2-benzenedicarboxylic or simply phthalic acid) starting around 200 °C leads to the formation of phthalic anhydride by the reaction:



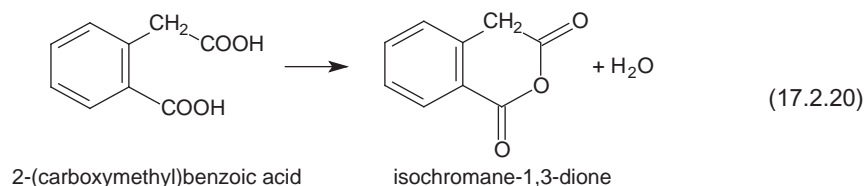
Substituted *o*-phthalic acids with groups like alkyl, carboxyl, nitro, etc. undergo similar reactions to that of *o*-phthalic acid.

When the steric conditions are not favorable, the pyrolysis leads to decarboxylation for compounds with the COOH groups on a carbon aromatic ring. This is, for example, the case of isophthalic acid (1,3-benzenedicarboxylic acid), which does not form an anhydride upon heating. At temperatures higher than 450 °C, a decarboxylation process starts with the formation of CO<sub>2</sub>, benzoic acid, and benzene. Besides the formation of CO<sub>2</sub> during thermal decomposition, the formation of CO has been reported [35].



Terephthalic acid (1,4-benzenedicarboxylic acid) is also stable and sublimes without decomposition when heated above 300 °C. Above 450 °C, depending on the heating time, it behaves similarly to isophthalic acid [36].

The formation of anhydrides from dicarboxylic acids with the COOH groups in vicinal position on a carbon aromatic ring is favored when steric conditions are favorable and is similar to the case of formation of an anhydride from succinic acid. The same process of formation of anhydrides takes place when the two carboxyl groups are in  $\gamma$ -position and the steric conditions are favorable. For example, naphthalene-1,8-dicarboxylic acid, naphthalene-1,4,5,8-tetracarboxylic acid, and 2-(carboxymethyl)benzoic acid easily form anhydrides as shown below for 2-(carboxymethyl)benzoic acid:



In contrast, the carboxyl groups on  $\beta$ - or  $\gamma$ -positions on a heterocyclic aromatic ring typically do not generate anhydrides, even when steric conditions are favorable. For example, pyridine-3,4-dicarboxylic acid (cincomeronic acid) does not form an anhydride upon heating and undergoes a decarboxylation



O=C(O)c1ccncc1C(=O)O  
 cincomeronic acid

$\xrightarrow{-\text{CO}_2}$

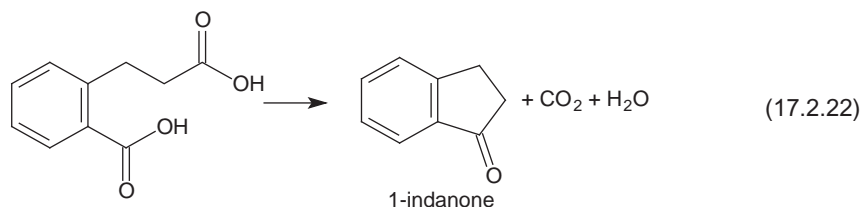
O=C(O)c1cccnc1  
 4-pyridincarboxylic  
acid

+

O=C(O)c1ccccn1  
 3-pyridincarboxylic  
acid

(17.2.21)

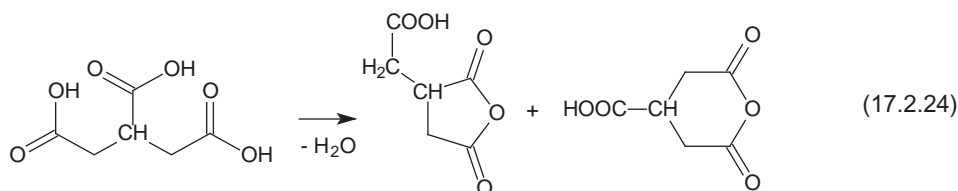
Acids with a carbon aromatic ring that contain a structure similar to adipic acid behave similarly to adipic acid and generate ketones. For example, 2-(2-carboxyethyl)-benzoic acid easily forms upon heating 1-indanone, as shown in the following reaction:


$$\text{C}_6\text{H}_4(\text{COOH})_2 \rightarrow \text{C}_{12}\text{H}_8\text{O} + \text{H}_2\text{O} + \text{CO}_2 \quad (17.2.23)$$

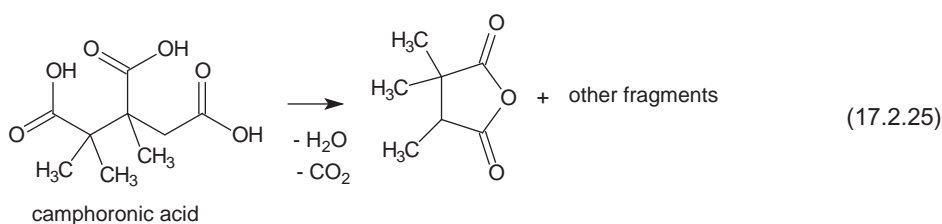
### **Polycarboxylic acids**

The presence of more than two carboxyl groups in an acid molecule does not affect significantly the outcome of pyrolysis as compared to the result from a dibasic acid. Depending on the position of the carboxyl groups, one of these may appear to act independently (and can suffer further pyrolysis). For example, propan-1,2,3-tricarboxylic acid (tricarballic acid) generates when heated a mixture of

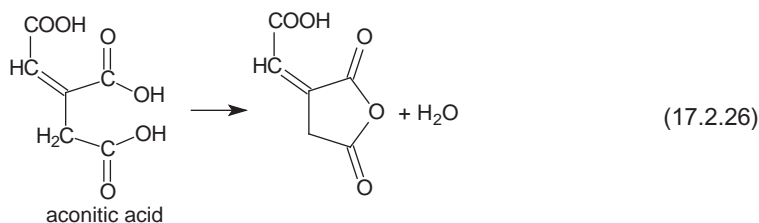
anhydrides shown as follows:



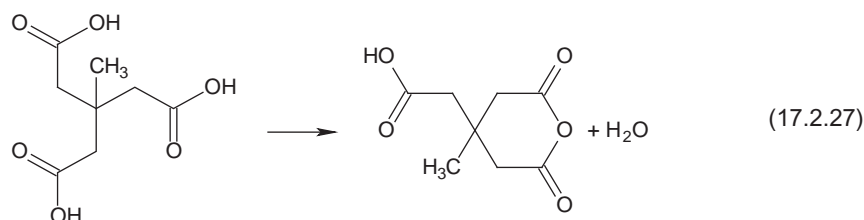
Further thermal decomposition of the anhydrides formed in the first step of pyrolysis typically leads to decarboxylation reactions. One such example is the decomposition of 1,1,3-trimethylpropane-1,2,3-tricarboxylic acid (camphoronic acid):



Another example of tricarboxylic acid is aconitic acid, which by thermal decomposition around 140 °C forms an anhydride similar to succinic acid as shown below:

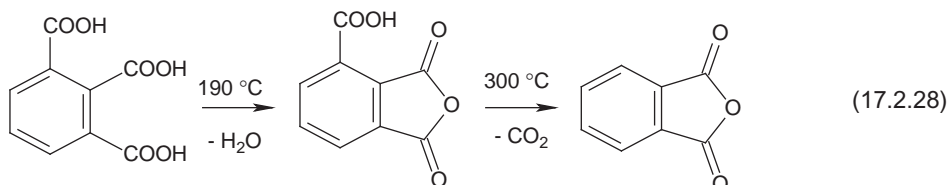


Formation of anhydrides takes place, as well, from tricarboxylic acids that have a moiety similar to glutaric acid, like 2-(carboxymethyl)-2-methylpropane-1,3-dicarboxylic acid shown below:



The formation of an anhydride with the preservation of one of the carboxyl groups also occurs during thermal decomposition of benzene-1,2,3-tricarboxylic acid (hemimellitic acid). Thermal decomposition at temperatures higher than 300 °C leads to the decarboxylation and formation of phthalic anhydride, as

shown in the reactions below:



Similarly, naphthalene-1,4,5,8 tetracarboxylic acid forms a dianhydride when heated for extended time around 150 °C (1–2 h). The dianhydride is the main pyrolysis product even when thermal decomposition takes place at higher temperatures.

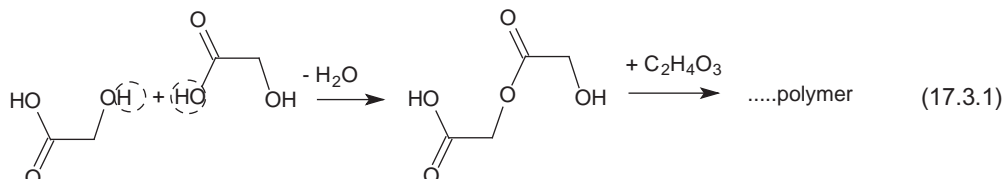
### 17.3. HYDROXY ACIDS

#### General aspects

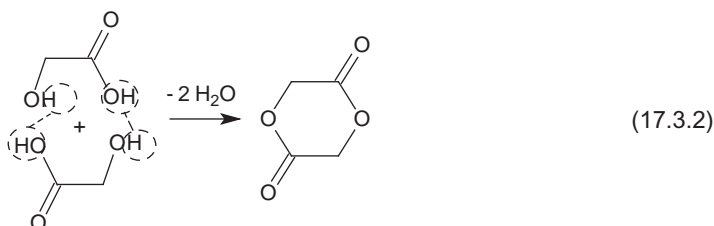
Hydroxy acids are compounds containing in their structure both carboxyl and hydroxyl groups. Depending on the position of the two groups (OH and COOH), hydroxy acids are classified as  $\alpha$ -hydroxy acids (the COOH and OH attached on the same carbon),  $\beta$ -hydroxy acids,  $\gamma$ -hydroxy acids, etc. A large number of hydroxy acids are found in nature. Some of these acids are related to carbohydrates. Sugar acids include aldonic acids generated by the direct oxidation of the aldehyde group from a saccharide, aldonic acids generated by the transformation of the aldehyde group and of the terminal CH<sub>2</sub>OH group of a saccharide into COOH, ketoaldonic acids, and saccharinic acids. Uronic acids are also hydroxy acids, and a discussion regarding their pyrolysis was included in Section 16.3 since these acids have a structure closer to that of carbohydrates.

#### $\alpha$ -Hydroxy acids

Depending of the acid structure, several reaction paths are possible during pyrolysis of  $\alpha$ -hydroxy acids. For the simplest acid from this class, glycolic acid, the first effect of increased temperatures in the range 240–280 °C is the formation of an ester by the elimination of water between two glycolic acid molecules. The condensation reaction continues between the ester (which has two reactive groups at the end of the chain) and new molecules of glycolic acid. The final result is the formation of a polymer shown as follows:

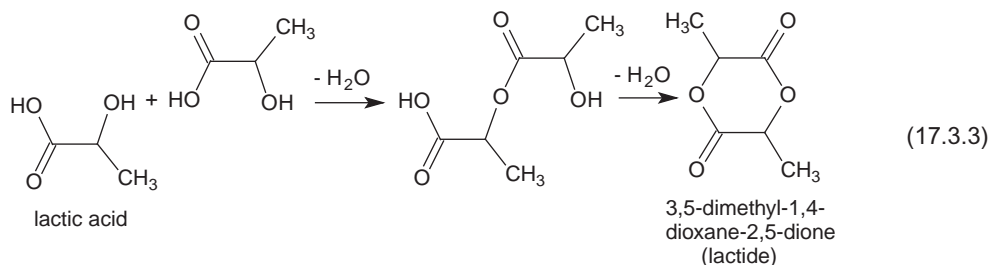


When heating is associated with vacuum even at lower temperatures than required for the polymer formation, two water molecules are eliminated from two glycolic acid molecules and the reaction leads to a dimer (1,4-dioxane-2,5-dione) as follows:



Pyrolysis at higher temperatures of glycolic acid, of its polymer, or of the dimer leads to decomposition with the formation of small molecules such as  $\text{H}_2\text{O}$ ,  $\text{CO}$ , char, and other compounds such as hydroxyacetaldehyde.

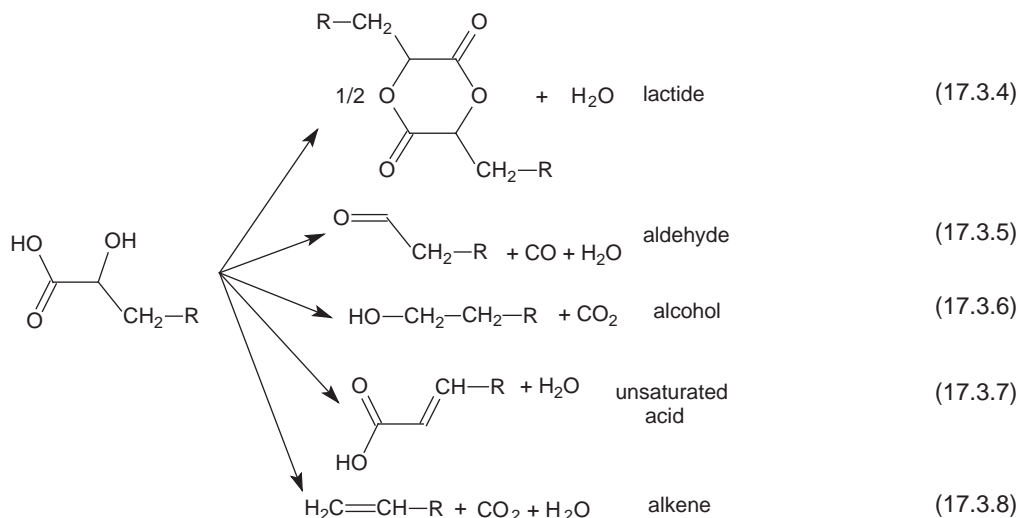
Lactic acid (2-hydroxypropanoic acid) behaves similarly to glycolic acid. The first step during heating around  $140^\circ\text{C}$  is the formation of an ester, but the reaction continues when heating is performed at temperatures higher than  $150^\circ\text{C}$  with the formation of a double ester between two lactic acid molecules. The resulting compound, 3,5-dimethyl-1,4-dioxane-2,5-dione, is also named a lactide. The reactions are shown below:



Continuing the heating, but in the presence of a catalyst such as certain Sn salts (e.g., octanoate), the lactide is transformed into a polymer. Pyrolysis of polylactic acid generates mainly  $\text{CO}$  and acetaldehyde, but also a number of other small molecules [37]. Flash pyrolysis of lactic acid also generates  $\text{CO}$ ,  $\text{CO}_2$ , and acetaldehyde.

Several other  $\alpha$ -hydroxy acids behave similarly to lactic acid. Examples include 2-hydroxy-3-methylbutanoic acid and 2-hydroxy-4-methylpentanoic acid. These acids form upon heating a lactide type compound that decomposes to various fragments at higher temperatures.

Depending on individual structure, besides reactions with the formation of 1,4-dioxane-2,5-diones (lactides),  $\alpha$ -hydroxy acids can undergo other types of reactions. These include formation of aldehydes by the elimination of  $\text{CO}$  and  $\text{H}_2\text{O}$ , formation of alcohols by the elimination of  $\text{CO}_2$ , formation of unsaturated acids by the elimination of water, and formation of alkenes by the elimination of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . All these possible reactions are shown below:



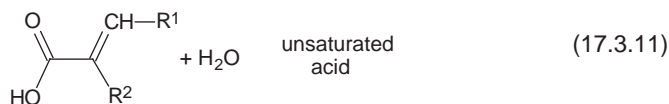
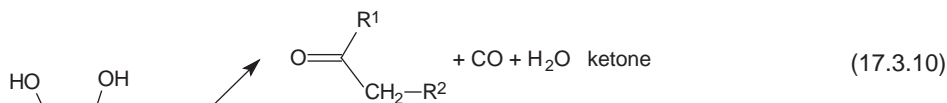
As an example,  $\alpha$ -hydroxyheptanoic acid heated around  $300^\circ\text{C}$  generates a mixture of a substituted 1,4-dioxane-2,5-dione (reaction 17.3.4), caproic aldehyde with elimination of  $\text{CO}$  and  $\text{H}_2\text{O}$  (reaction 17.3.5), 2-heptenoic acid (reaction 17.3.7), and 1-hexene (reaction 17.3.8). Formation of aldehydes

(reaction 17.3.5) typically is seen for longer hydrocarbon chain acids, like  $\alpha$ -hydroxypalmitic acid, which around 170 °C and in vacuum (20–25 Torr) generates pentadecyl aldehyde [38].  $\alpha$ -Hydroxystearic acid also forms the C<sub>15</sub> *n*-aldehyde with a 60% yield [39]. Mandelic acid in the temperature range 300–340 °C and 15–52 Torr also generates benzaldehyde (by reaction 17.3.5), CO, and H<sub>2</sub>O, as well as small amounts of benzyl alcohol and CO<sub>2</sub> (by reaction 17.3.6) [40]. The reaction for mandelic acid decomposition in gas phase was found to be unimolecular, having the following Arrhenius equation [41]:

$$\log_{10} k \text{ (s}^{-1}\text{)} = (12.54 \pm 0.12) - \frac{(171.3 \pm 1.4) \text{ kJ/mol}}{2.303 RT} \quad (17.3.9)$$

In different pyrolysis conditions, for example, by heating mandelic acid at 250 °C for an extended period of time, phenyl acetic acid, diphenylmaleic anhydride, and small levels of other molecules are obtained. The formation of phenyl acetic acid can be explained by various oxidation–reduction reactions that may occur during pyrolysis [13]. The mechanisms for the formation of aldehyde by reaction 17.3.5 may involve an initial step of lactide formation followed by CO elimination.

For the case of an OH group substituted to a tertiary carbon, all the reactions 17.3.4 through 17.3.8 are still possible (ketone being formed instead of an aldehyde in reaction 17.3.5). However, the water elimination is favored. As a result, the preferred reactions are the following:

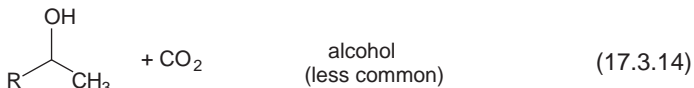
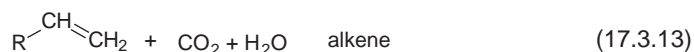
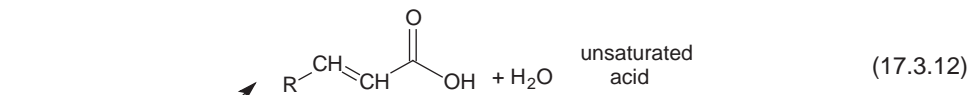


As an example, 2-hydroxy-2-methylpropanoic acid when heated at about 210 °C generates some lactide, about 33% methacrylic acid, and about 48% acetone [13].

Substitution with aryl radicals at the carbon bearing the OH group does not modify the general scheme of  $\alpha$ -hydroxy acid decomposition (although variations are seen for particular acids). For example, 2-hydroxy-2,2-diphenylacetic acid decomposes around 180 °C, following in part reaction 17.3.10 with the formation of benzophenone, but also with the formation of diphenylacetic acid, CO<sub>2</sub>, and other fragment molecules.

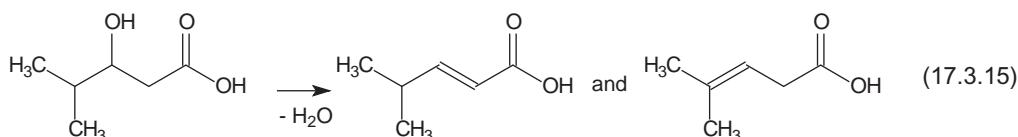
### $\beta$ -Hydroxy acids

$\beta$ -Hydroxy acids pyrolysis may take several routes depending on the acid structure. When hydrogen atoms are available on the  $\alpha$ -carbon, the following reactions are possible:

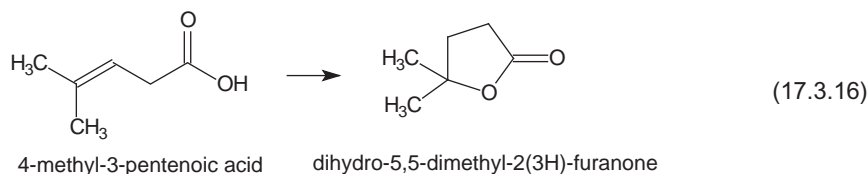


One example of a  $\beta$ -hydroxy acid is 3-hydroxybutanoic acid, which at 180 °C loses water to form 2-butenic acid, following a reaction of the type 17.3.12. A similar behavior is seen for 3-hydroxypentanoic acid. The formation of alkenes during pyrolysis is also a common reaction, but the formation of an alcohol by reaction 17.3.4 is less common.

The water elimination by pyrolysis of  $\beta$ -unsaturated acids has been associated for some compounds with a migration of the double bond, as shown in the reaction below for 3-hydroxy-4-methylpentanoic acid:

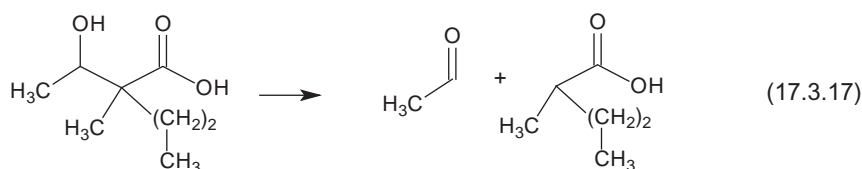


The elimination of water with the formation of a double bond can be associated with a lactone formation when sterically possible. This reaction is shown as follows for 4-methyl-3-pentenoic acid:

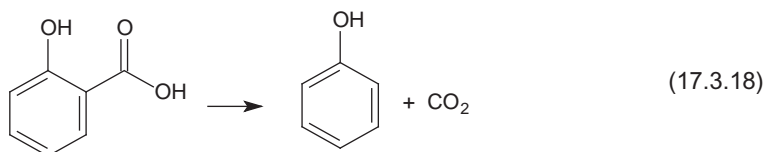


The lactone dihydro-5,5-dimethyl-2(3H)-furanone is found in the pyrolysate of 3-hydroxy-4-methylpentanoic acid together with the two 4-methylpentenoic acids. The corresponding alkenes (following reaction 17.3.13) also are found in the pyrolysate.

In the case of aliphatic  $\beta$ -hydroxy acids having no hydrogen atoms on the  $\alpha$ -carbon, the decomposition reactions include decarboxylations and fragmentations of the molecule with the formation of an aldehyde, as seen for some secondary alcohols (see, e.g., reaction 9.1.13). An example of this type of decomposition is shown below for 2-(hydroxyethyl)-2-methylpentanoic acid:

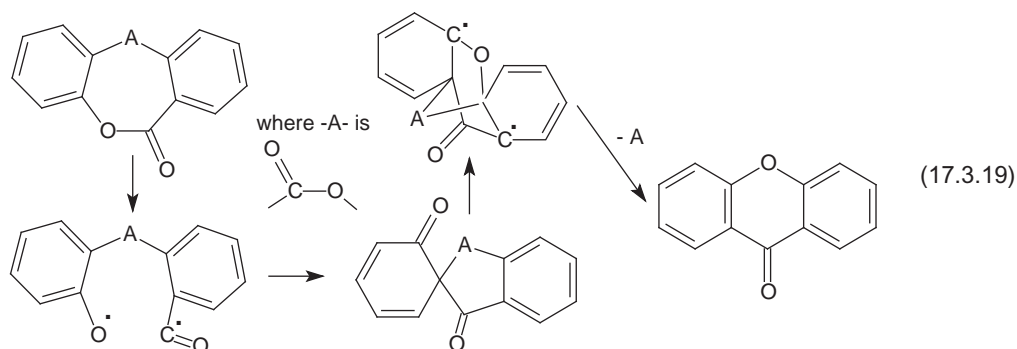


Some  $\beta$ -hydroxy acids contain the OH and COOH groups attached to an aromatic ring. One example is salicylic acid, which decomposes following a reaction similar to reaction 7.3.14, leading to the formation of phenol at temperatures above 350 °C:



Phenol is not generated directly at temperatures below 280 °C, and the formation of phenyl salicylate with CO<sub>2</sub> and H<sub>2</sub>O elimination is noticed. A by-product of phenyl salicylate pyrolysis is xanthone. The formation of xanthone may go through the intermediate formation of a disalicylide (salicylic acid

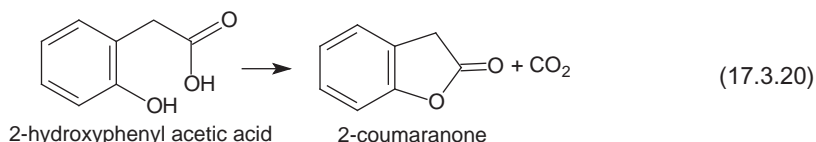
bimolecular cyclic ester, or dibenzo[*c,g*]1,5-dioxocin-6,12-dione) in a sequence of reactions as shown below:



The proposed mechanism for reaction 17.3.19 is similar to reaction 2.4.6 and would be expected to be regiospecific for a substituted salicylic acid [42]. A separate experiment with the pyrolysis of the disalicylide led to  $\text{CO}_2$  elimination and formation of xanthone [13].

### ***γ-Hydroxy acids and δ-hydroxy acids***

The aliphatic  $\gamma$ -hydroxy acids and  $\delta$ -hydroxy acids are typically unstable compounds that easily change into lactones. The acids with the OH on an aromatic ring are more stable, and they also form lactones upon heating at temperatures as low as 100 °C. The reaction is shown below for 2-hydroxyphenylacetic acid, which generates 2-coumaranone:



The resulting lactone is highly stable at elevated temperatures. The formation of lactones from  $\gamma$ - and  $\delta$ -hydroxy acids is a common reaction caused by the particular stability of five- and six-atom rings. The reaction frequently is encountered during heating of many complex compounds that may contain other functional groups besides OH and COOH.

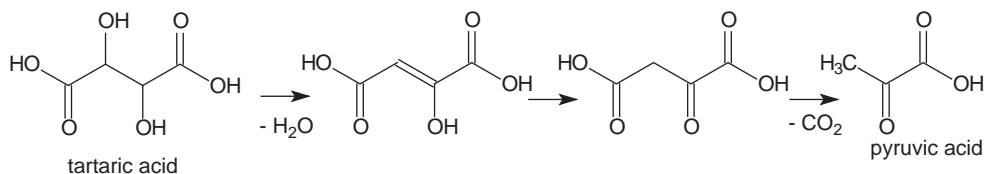
### ***Hydroxy acids with several hydroxyl and/or carboxyl groups***

Many organic acids having more than one OH and more than one COOH groups are commonly found in plants and animals. Examples include citric acid (an intermediate in the metabolism of all living cells that use oxygen), tartaric acid (common in many plants and in food), mucic acid (which is an oxidation product of hexoses), etc.

Pyrolysis of more complex acids usually takes place by reactions similar to simpler acids, combining various possibilities of elimination of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}+\text{CO}_2$ , and in some instances CO. Many sugar acids can be included in this group of compounds. Pyrolysis of aldonic acids starts with the formation of lactones. Some of these acids, such as gluconic acid or ribonic acid, form lactones even when their solutions in water are evaporated. Further decomposition of these lactones leads to  $\text{CO}_2$  and water elimination, with the formation of furan (furanones) and pyran (pyranones) derivatives [43]. Pyrolysis of 3-deoxyaldonic acids is not different from that of aldonic acids. The missing OH group from the carbon chain being in  $\beta$ -position to the carboxyl group, the formation of lactones is not affected. Some

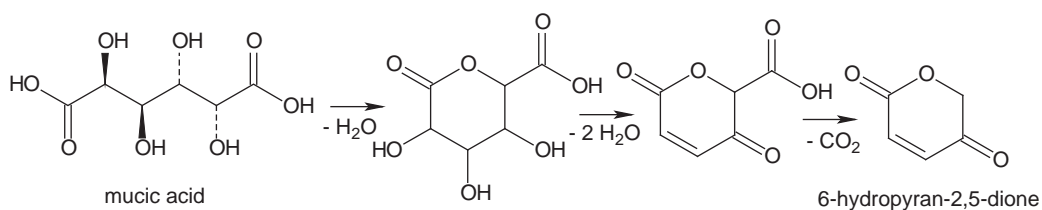
examples of pyrolysis for several more common hydroxy acids with multiple OH and COOH groups are given below.

Tartaric acid  $\text{HOOC}-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{COOH}$  has two OH and two COOH groups and can be considered an aldaric acid from erythrose. The acid contains two chiral carbons forming three stereoisomers (dextrotartaric, levotartaric, and mesotartaric acid). Mesotartaric acid upon heating around  $200^\circ\text{C}$  decomposes in part and also changes into a mixture of the other two acids. The first stage during heating of tartaric acid around  $165^\circ\text{C}$  in vacuum is the formation of a lactide type compound. Further decomposition generates mainly  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}-\text{COOH}$ ,  $\text{CH}_3-\text{COOH}$ , and  $\text{CH}_3-\text{C}(\text{O})-\text{COOH}$ . The formation of pyruvic acid can be explained by the following set of reactions:

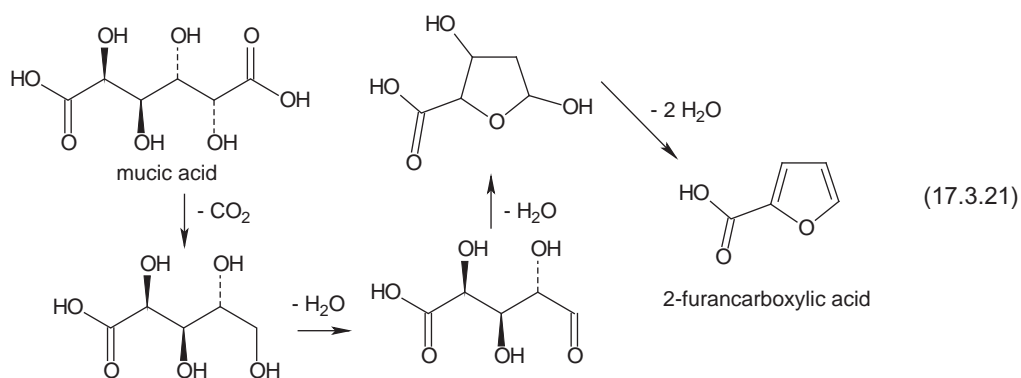


Mucic acid contains four OH groups and two COOH groups being an aldaric acid, (2*S*,3*R*, 4*S*,5*R*)-2,3,4,5-tetrahydroxyhexandioic acid, derived from galactose. Its structure is very similar to that of glucaric acid (see Section 16.3). Pyrolysis of 1.0 mg of this acid was performed in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C}/\text{ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ . The pyrolysate was analyzed under conditions given in Table 4.6.1. The pyrogram is shown in Figure 17.3.1. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 17.3.1. The evaluation of the mole percent was obtained based solely on peak areas.

Under these experimental conditions, the main pyrolysis products are  $\text{CO}_2$ , furan, 2-furancarboxylic acid, and 6-hydropyran-2,5-dione. The formation of pyran derivatives in the final pyrolysis product is very likely the result of initial formation of lactones, as shown in the following chain of reaction explaining the formation of 6-hydropyran-2,5-dione:



The formation of furan derivatives could be the result of an initial decarboxylation followed by water elimination. The following model reactions may explain the formation of 2-furancarboxylic acid:





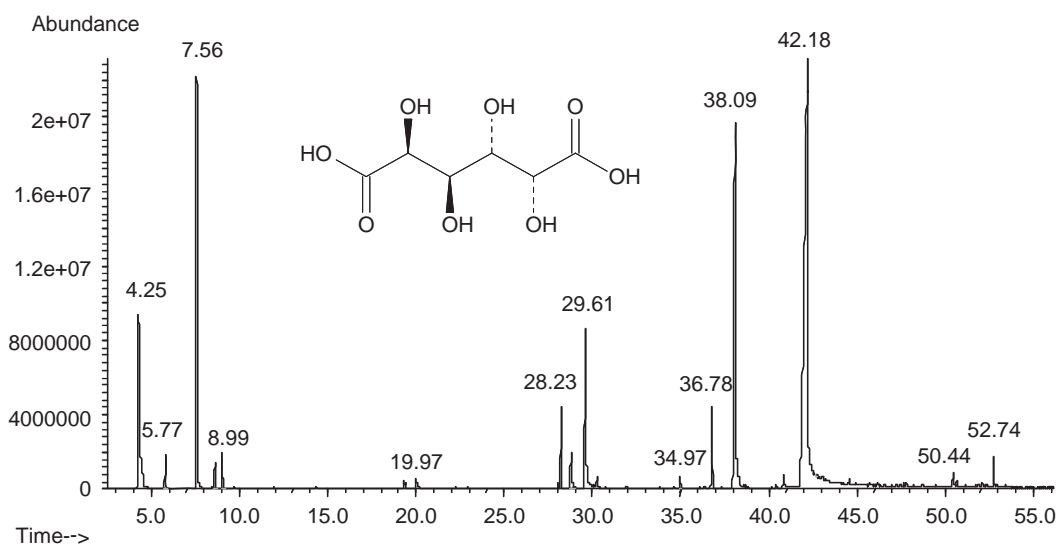


FIGURE 17.3.1. Pyrogram of mucic acid at 900°C. Peak assignment is given in Table 17.3.1 based on retention times.

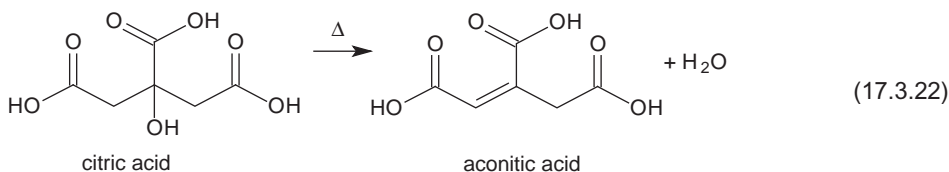
TABLE 17.3.1. Identification of the main peaks in the chromatogram shown in Figure 17.3.1 for the pyrolysis of mucic acid at 900°C (hydrogen, methane, ethylene, water were not analyzed due to the mass spectrometer settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Carbon dioxide	4.25	44	124-38-9	<b>20.57</b>
2	Acetaldehyde	5.77	44	75-07-0	1.56
3	Furan	7.56	68	110-00-9	<b>14.16</b>
4	2-Propenal (acrolein)	8.60	56	107-02-8	1.09
5	Acetone	8.99	58	67-64-1	1.53
6	2-Butenal (Z)	19.28	70	15798-64-8	0.20
7	2-Methyl-2-propenal	19.38	70	78-85-3	0.13
8	Acetic acid	19.97	60	64-19-7	0.84
9	(E) 2-Methyl-2-butenal	28.02	84	1115-11-3	0.11
10	(Z) 2-Methyl-2-butenal	28.23	84	N/A	2.15
11	(2H)-Furan-3-one	28.79	84	N/A	1.34
12	Butandial	29.61	86	638-37-9	6.52
13	Furancarboxaldehyde (furfural)	30.26	96	98-01-1	0.27
14	Benzofuran	34.97	118	271-89-6	0.23
15	2(5H)-Furanone	36.78	84	497-23-4	2.52
16	6-Hydropyran-2,5-dione	38.09	112	N/A	<b>13.46</b>
17	Propionic acid	40.83	74	79-09-4	0.58
18	2-Furancarboxylic acid	42.18	112	88-14-2	<b>32.05</b>
19	Dihydro-2,5-furandione	42.68	100	108-30-5	0.03
20	Furancarboxylic acid -2-ethyl ester?	50.44	140	614-99-3	0.30
21	Furancarboxylic acid 2-propenyl ester?	52.74	152	4208-49-5	0.36

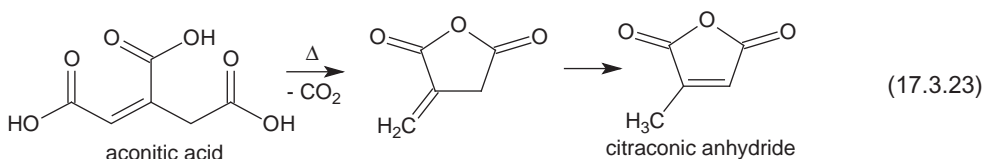
Note: Numbers in bold indicate the major pyrolysis constituents.

As in many other pyrolytic reactions, the compounds generated in the pyrolysate are those with higher thermal stability. This explains the formation of furan and pyran cycles.

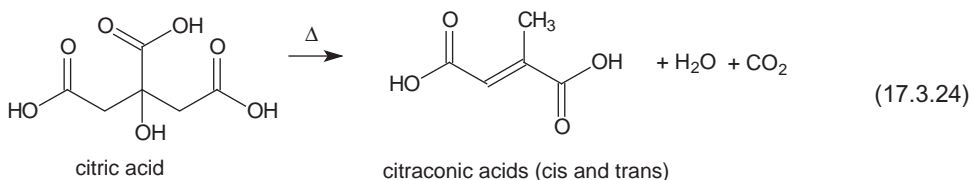
Another common hydroxy acid containing three carboxyl groups and one OH group is citric acid. When heated at lower temperatures, around 175 °C and for longer time (1–2 h), citric acid generates aconitic acid, as shown below:



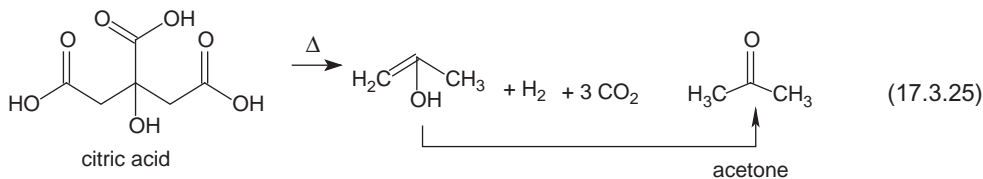
Further heating of aconitic acid leads to the formation of itaconic anhydride (3-methylene-4-hydrofuran-2,5-dione), which isomerizes into citraconic anhydride (3-methyl-2,5-furandione):



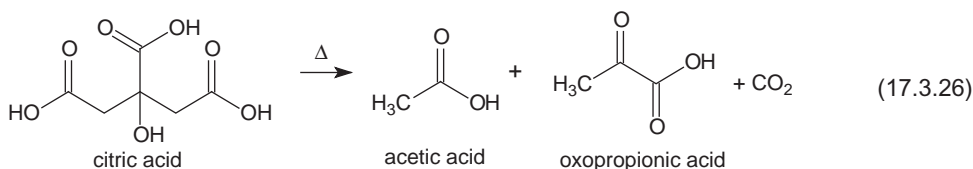
During flash pyrolysis in helium at 700 °C, the main products (over 90%) of citric acid include citraconic anhydride, citraconic acids (*cis* and *trans*), and propanone together with H<sub>2</sub>O and CO<sub>2</sub>. The formation of citraconic acid can be the result of a reaction between water present in the pyrolysate and citraconic anhydride after the pyrolysis took place. The overall reaction leading to citraconic acids from citric acid can be written as follows:

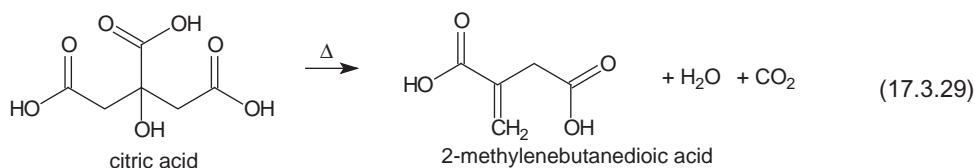
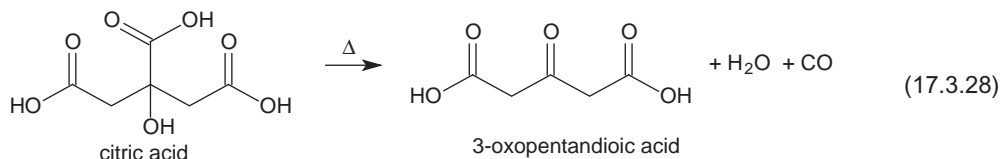
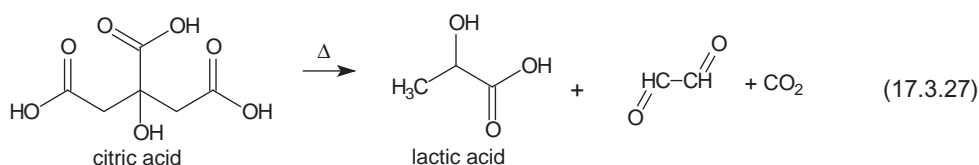


The reaction leading to the formation of acetone is indicated as follows:



Other compounds at lower levels are also detected in the pyrolysate. The formation of some of these compounds is shown below:





The formation of 2-methylenebutanedioic acid can be explained by the hydrolysis of itaconic anhydride. A very detailed analysis of pyrolysis products of citric acid indicates traces of many other compounds.

Quinic acid or (1*S*,3*R*,4*S*,5*R*)-1,3,4,5-tetrahydroxycyclohexancarboxylic acid contains four OH groups and a carboxyl group on a cyclohexane skeleton. This acid is found in coffee and other plant products. The molecule has four chiral centers and therefore several stereoisomers. Pyrolysis of 1.0 mg of quinic acid was performed in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ . The pyrolysate was analyzed under conditions given in Table 4.6.1. The pyrogram is shown in Figure 17.3.2. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 17.3.2. The evaluation of the mole percent was obtained based solely on peak areas.

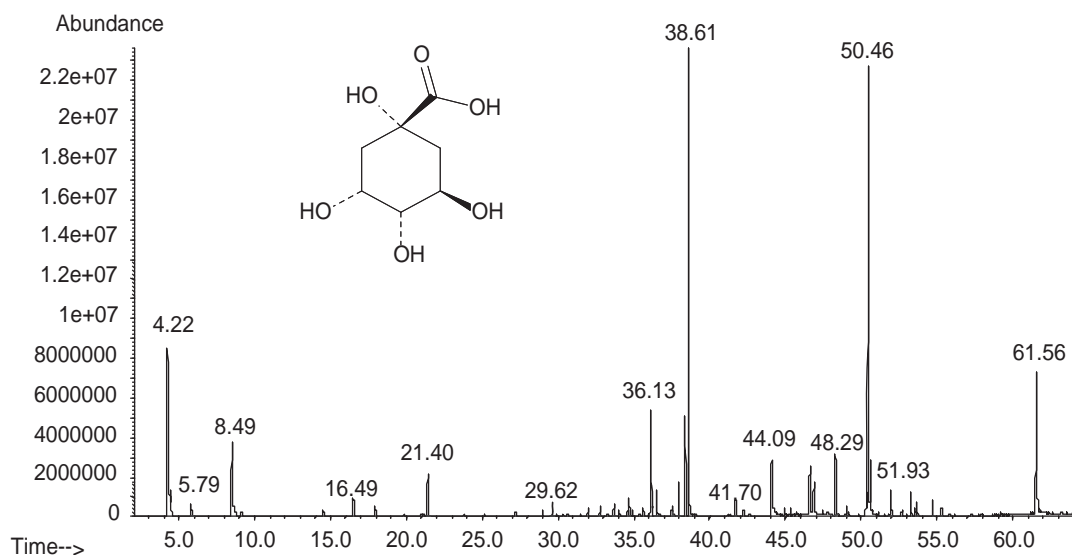


FIGURE 17.3.2. Pyrogram of quinic acid at  $900^\circ\text{C}$ . Peak assignment is given in Table 17.3.2 based on retention times.

TABLE 17.3.2. Identification of the main peaks in the chromatogram shown in Figure 17.3.2 for the pyrolysis of quinic acid at 900°C (hydrogen, methane, ethylene, and water were not analyzed due to the mass spectrometer settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Carbon dioxide	4.22	44	124-38-9	<b>24.44</b>
2	Acetaldehyde	5.79	44	75-07-0	1.58
3	1,3-Cyclopentadiene	8.49	66	542-92-7	5.02
4	Acetone	9.11	58	67-64-1	0.53
5	2,3-Butanedione (diacetyl)	14.48	86	431-03-8	0.58
6	Benzene	16.49	78	71-43-2	1.52
7	Hydroxyacetaldehyde (glycol aldehyde)	17.90	60	141-46-8	1.12
8	2,3-Dihydrofuran	19.87	70	N/A	0.44
9	Vinylfuran	21.40	94	1487-18-9	2.08
10	Crotonic acid vinyl ester	28.95	112	14861-06-4	0.45
11	2-Butenoic acid	29.62	86	107-93-7	0.55
12	2-Cyclopenten-2-one	30.64	82	930-30-3	0.34
13	2-Methyl-2-cyclopentene-1-one	32.76	96	1120-73-6	0.32
14	2-Butenoic acid methyl ester	33.68	100	623-43-8	0.41
15	2,4-Hexadienoic acid	34.00	112	110-44-1	0.28
16	3-Methylene-dihydro-2(3H)-furanone	34.58	98	547-65-9	0.42
17	3,5-Dimethyl-2(5H)-furanone	34.69	112	N/A	0.48
18	2,4-Hexadienoic acid (sorbic acid)	34.94	112	110-44-1	0.28
19	5-Methyl-2-furancarboxaldehyde	35.61	110	620-02-0	0.28
20	4-Hydroxy-2-cyclohexen-1-one	36.13	112	30182-12-8	2.94
21	1,2-Cyclohexanedione	36.53	112	765-87-7	0.67
22	3-Methylene-dihydro-2,5-furandione	37.49	112	3/8/2170	0.28
23	3-Methyl-1,2-cyclopentanedione	37.56	112	765-70-8	0.32
24	2-Hydroxy-3-methyl-2-cyclopenten-1-one (cyclovene)	37.95	112	80-71-7	0.89
25	3-Methyl-2,5-furandione (citraconic acid anhydride)	38.39	112	N/A	2.89
26	Phenol	38.61	94	108-95-2	<b>16.75</b>
27	Cyclohexanecarboxaldehyde	41.70	112	2043-61-0	0.47
28	3-Methyl-3,4-dihydro-2,5-furandione	42.21	114	4100-80-5	0.32
29	Benzoic acid	44.09	122	65-85-0	<b>2.72</b>
30	2-Butenoic acid (crotonic acid)	46.60	86	107-93-7	2.91
31	Unknown	46.86	114	N/A	0.88
32	1-(5-Methyl-2-furyl)-1-propanone	48.29	138	10599-69-6	1.53
33	Unknown	49.00	140	N/A	0.19
34	Unknown	50.31	140	N/A	0.51

(Continued)

TABLE 17.3.2. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
35	Hydroquinone	50.46	110	123-31-9	<b>18.04</b>
36	2,5-Dioxacyclohexanecarboxylic acid	50.61	156	N/A	1.17
37	4-Hydroxy-??-dimethyl-cyclohex-2-en-1-one	51.93	140	N/A	0.77
38	Unknown	53.27	140?	N/A	0.47
39	Unknown	53.68	140	N/A	0.28
40	Unknown	54.71	198	N/A	0.22
41	1,2,3,5-Cyclohexanetetraol	61.56	148	53585-08-3	3.70

Note: Numbers in bold indicate the major pyrolysis constituents.

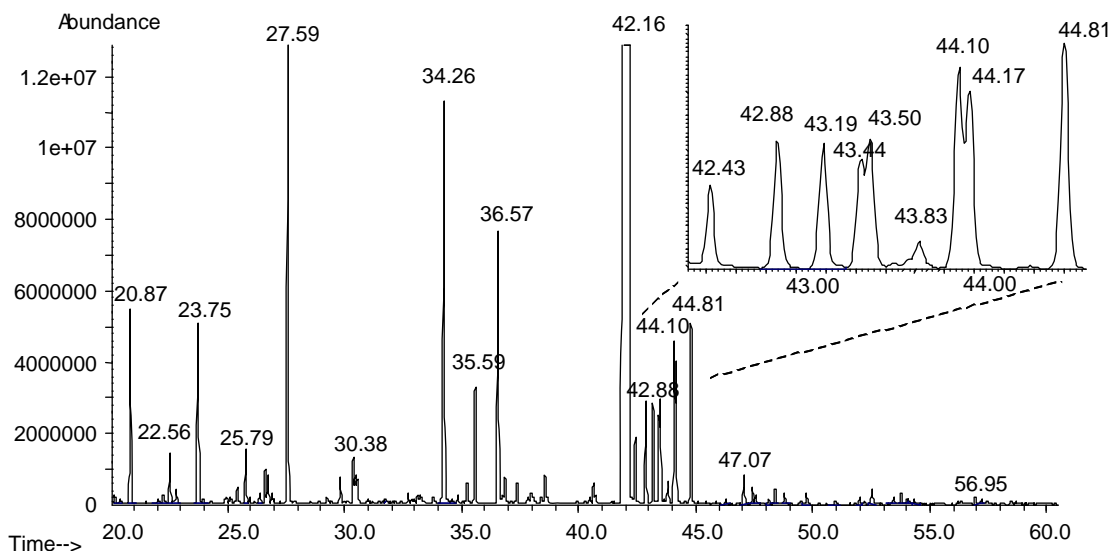


FIGURE 17.3.3. Window (20.0–60.0 min) from the chromatogram of TMS derivative of a pyrolysate of quinic acid at 900 °C (enlarged range 42–45 min). Peak assignment is given in Table 17.3.3 based on retention times.

As shown in Table 17.3.2, the main pyrolysis products of quinic acid are CO<sub>2</sub>, phenol, and hydroquinone. However, since quinic acid contains four OH group and one COOH group, it is likely that some of the pyrolysis products will contain compounds with several OH groups (and possibly a COOH group) and, having a high polarity, will not elute from the chromatographic column in the conditions described in Table 4.6.1. For this reason, quinic acid was pyrolyzed and analyzed off-line after the silylation of the pyrolysate to trimethylsilyl (TMS) derivatives using BSTFA in DMF (see Table 4.6.2). The time window between 20.0 min and 60.0 min of the resulting chromatogram is shown in Figure 17.3.3, with peak identification given in Table 17.3.3. The first part of the chromatogram from Figure 17.3.3 shows compounds already identified by online pyrolysis and described in Table 17.3.2.

In addition to the compounds identified in Table 17.3.2, one more pyrolysis product of quinic acid is shown in Table 17.3.3. This product is quinic acid  $\gamma$ -lactone (2,3,5-trihydroxy-7-oxabicyclo[3.2.1]octan-6-one). The presence of catechol in the pyrolysate was also detected in the silylated pyrolysate,

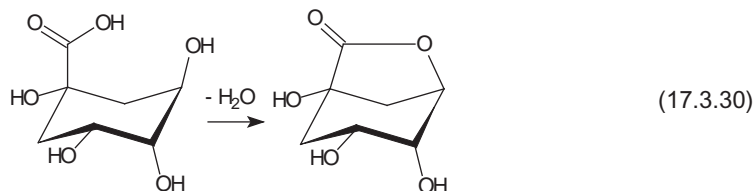
TABLE 17.3.3. Identification of the main peaks in the chromatogram shown in Figure 17.3.3 for the pyrolysate of quinic acid derivatized with bis(trimethylsilyl)trifluoro-acetamide (BSTFA) and their molar level relative to quinic acid  $\gamma$ -lactone 3 TMS

No.	Compound	Ret. time	MW	Fragment ions m/z (intensity)	Mole percent lactone
1	Benzoic acid TMS	20.87	194	179(100), 105(55), 135(43), 77(32), 194(8)	<b>6.09</b>
2	2,6-Dihydroxy-1,4-dioxane 2 TMS	22.56	264	117(100), 73(84), 161(60), 101(50), 191(23)	1.18
3	Catechol 2 TMS	23.75	154	73(100), 254(46), 239(9), 151(8), 255(8)	<b>8.45</b>
4	Unknown	25.79	236	147(100), 73(100), 221(20)	1.30
5	4-Methylcatechol 2 TMS	26.92	268	73(100), 268(55), 253(10)	0.33
6	Hydroquinone 2 TMS	27.60	254	239(100), 254(82), 73(18), 112(10)	<b>11.76</b>
7	Unknown	30.38	272	156(100), 73(75), 147(30), 257(4), 272(1)	1.00
8	3-Hydroxybenzoic acid 2 TMS	34.27	282	267(100), 282(45), 223(43), 193(40)	<b>9.72</b>
9	I.S.	35.59	310	310(100), 295(100), 73(45)	2.33
10	4-Hydroxybenzoic acid 2 TMS	36.57	282	267(100), 223(65), 193(55), 282(30)	<b>6.56</b>
11	Quinic acid $\gamma$ -lactone 3 TMS	42.16	390	73(100), 334(85), 204(72), 256(50), 375(15)	<b>100.0</b>
12	Quinic acid 1,4-lactone or $\gamma$ -lactone isomer 3 TMS	42.43	390	204(100), 73(92), 334(50), 375(30), 256(18)	1.02
13	1,2,4,5-Tetrahydroxycyclohexane 4 TMS	42.88	436	217(100) 73(25), 375(8), 257(7)	1.44
14	1,3,4,5-Tetrahydroxycyclohexane 4 TMS	43.19	436	217(100) 73(25), 375(23), 257(7)	1.42
15	Unknown	43.44	398	131(100), 73(33), 398(4), 383(4), 295(3)	1.25
16	4,5-Dihydroxy-2-cyclohexenecarboxylic acid 3 TMS	43.50	462	204(100), 73(75), 370(50), 193(48), 462(3)	1.32
17	Unknown	43.83	552	308(100), 73(50), 354(20), 267(20), 251(17)	0.35
18	Unknown	44.10	552	204(100), 73(46), 147(20), 357(6), 462(2)	1.75
19	Isomer quinic acid 5 TMS	44.17	552	73(100), 204(80), 334(75), 129(54), 347(4)	1.47
20	Quinic acid 5 TMS	44.81	552	345(100), 73(47), 255(33), 435(5), 462(2)	2.01
21	Unknown	47.07	552	73(100), 129(70), 103(33), 204(30), 364(20)	0.35
22	Unknown	56.95	552	73(100), 166(65), 257(35), 418(3)	0.11

Note: Numbers in bold indicate the major pyrolysis constituents.

although it was not detected by online pyrolysis procedure. The decarboxylation and water elimination processes easily explain the formation of these major compounds. Typical for pyrolysis, particularly at temperatures above 500–550 °C, the result consists mainly of thermally stable molecules including aromatic compounds. It is interesting to note that benzoic acid is also present in the pyrolysate (~2.7%), showing that some quinic acid molecules undergo water elimination without suffering

decarboxylation. The formation of quinic acid  $\gamma$ -lactone is shown in the following reaction:



Besides the main pyrolysis products, numerous small fragments including some aromatic compounds were present in the pyrolysate. Also, traces of compounds resulting from the condensation of two quinic acid molecules with different levels of dehydration and decarboxylation were detected. Char was also formed during quinic acid pyrolysis. The spectra of silylated quinic acid  $\gamma$ -lactone and of quinic acid are not available in common mass spectra libraries (up to NIST08) and are shown in Figures 17.3.4 and 17.3.5, respectively.

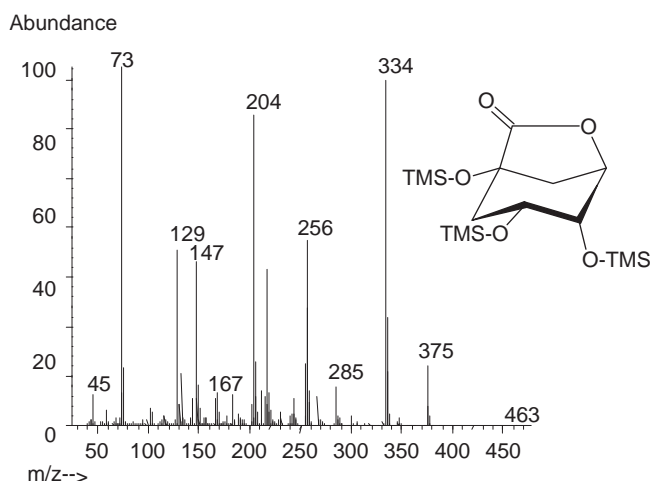


FIGURE 17.3.4. Mass spectrum of quinic acid  $\gamma$ -lactone 3 TMS.

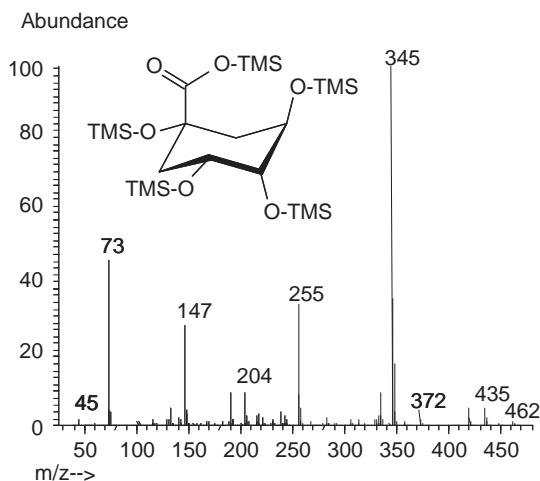
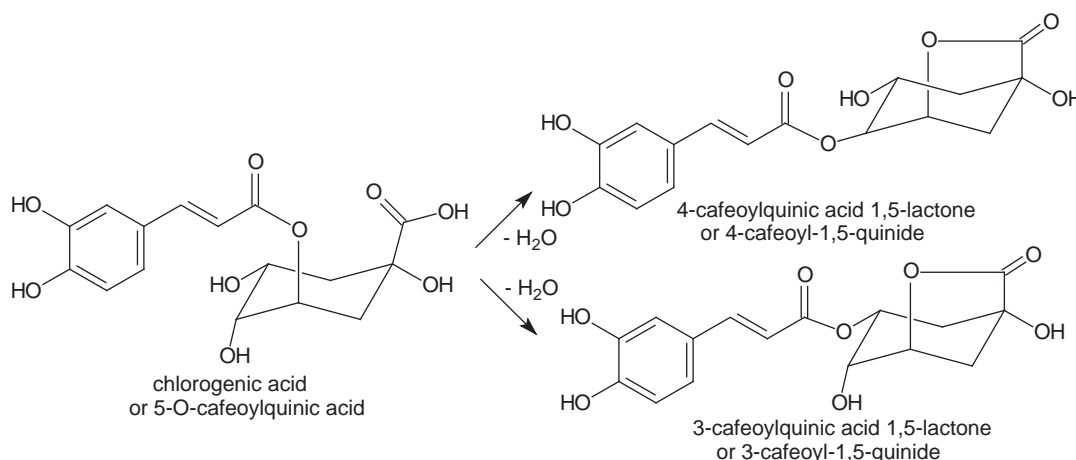


FIGURE 17.3.5. Mass spectrum of quinic acid 5 TMS.

Quinic acid in coffee is present mainly in the form of an ester with caffeic acid (*trans*-5-*O*-caffeoyl-*D*-quinic acid). This compound is known as chlorogenic acid. Chlorogenic acid is also present in tobacco and other plants. Because of its presence in materials typically subjected to elevated temperatures (roasting of coffee, burning of tobacco), pyrolysis of chlorogenic acid has been the subject of several studies [44–47].

Products of pyrolysis of chlorogenic acid are detected in roasted coffee [48]. The main compounds formed during coffee roasting are lactones formed from the quinic acid moiety. This type of reaction is shown below:



The lactones are formed in 1,5-position with the migration of the ester bond to caffeic acid to the position 3 (preferred) or 4 on the quinic acid molecule. The higher level of lactone present in coffee is 3-caffeoyl-1,5-quinide. It is likely that chlorogenic acid suffers initially an isomerization to 3-caffeoylquinic acid (or 4-caffeoylquinic acid) followed by dehydration. At higher temperatures, the molecule of chlorogenic acid starts decomposing. Pyrolysis of 1.0 mg of chlorogenic acid was performed in a Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900^{\circ}\text{C}$ ,  $\beta = 10^{\circ}\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280^{\circ}\text{C}$ . The pyrolysate was analyzed under conditions given in Table 4.6.1. The pyrogram is shown in Figure 17.3.6. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 17.3.4. Peak identification was done based on their mass spectrum, and the evaluation of the mole percent was obtained based on peak areas.

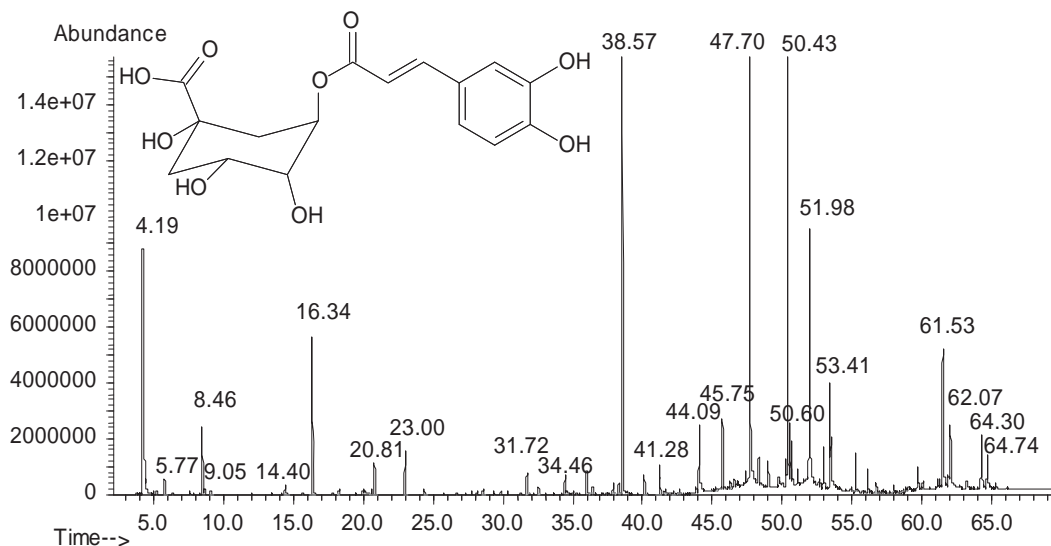


FIGURE 17.3.6. Pyrogram of chlorogenic acid at  $900^{\circ}\text{C}$ . Peak assignment in Table 17.3.4.



TABLE 17.3.4. Identification of the main peaks in the chromatogram shown in Figure 17.3.6 for the pyrolysis of chlorogenic acid at 900 °C (hydrogen, methane, ethylene, water were not analyzed due to the mass spectrometer settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Carbon dioxide	4.19	44	124-38-9	<b>25.41</b>
2	Acetaldehyde	5.77	44	75-07-0	0.65
3	1,3-Cyclopentadiene	8.46	66	542-92-7	2.39
4	Propanal	8.64	58	123-38-6	0.19
5	Acetone	9.05	58	67-64-1	0.15
6	2,3-Butanedione (diacetyl)	14.40	86	431-03-8	0.26
7	1-Methyl-1,3-cyclopentadiene	15.62	80	96-39-9	0.05
8	Benzene	16.34	78	71-43-2	<b>5.13</b>
9	2-Ethylfuran	18.26	96	3208-16-0	0.09
10	3-Methyl-3-buten-2-one	19.98	84	814-78-8	0.08
11	Acetic acid	20.08	60	64-19-7	0.33
12	1-Penten-2-one	20.37	84	1629-58-9	0.04
13	4-Penten-2-one	20.60	84	13891-87-7	0.10
14	Vinylfuran	20.81	94	1487-18-9	0.61
15	Toluene	23.00	92	108-88-3	0.86
16	3-Penten-2-one	24.38	84	625-33-2	0.11
17	Ethylbenzene	27.74	106	100-41-4	0.04
18	<i>p</i> -Xylene	28.16	106	106-42-3	0.05
19	Vinyl crotonate	28.59	112	14861-06-4	0.06
20	2-Methyl-2-propenoic acid	29.32	86	79-41-4	0.04
21	Styrene	29.86	104	100-42-5	0.04
22	2-Cyclopenten-1-one	30.34	82	930-30-3	0.05
23	2-Cyclopentene-1,4-dione	31.73	96	930-60-9	0.34
24	2-Methyl-2-cyclopenten-1-one	32.57	96	1120-73-6	0.14
25	2-Cyclohexen-1-one	34.46	96	930-68-7	0.39
26	2-Pentalenal	36.02	84	1576-87-0	0.58
27	1,2-Cyclohexanedione	36.44	112	765-87-7	0.13
28	2-Hydroxy-2-cyclopenten-1-one	37.93	112	80-71-7	0.31
29	3-Methyl-2,5-furandione	38.34	112	616-02-4	0.37
30	Phenol	38.57	94	108-95-2	<b>12.80</b>
31	2-Methylphenol	40.15	108	95-48-7	0.26
32	3-Methylphenol	41.22	108	108-39-4	0.10
33	4-Methylphenol	41.28	108	106-44-5	0.56
34	1,3-Benzodioxol-2-one	41.58	136	2171-74-6	0.03
35	5,6-Dihydro-2H-pyran-2-carboxaldehyde	41.71	112	53897-26-0	0.07
36	Dihydro-2H-pyran-2,6(3H)-dione	42.21	114	108-55-4	0.05
37	1,4-Cyclohexandione	42.65	112	637-88-7	0.10
38	2-Ethylphenol	43.86	122	123-07-9	0.10
39	Benzoic acid	44.09	122	65-85-0	1.75
40	5,5-Dimethyl-2(5H)-furanone	45.30	112	20019-64-1	0.05
41	2-Coumaranone	45.75	134	553-86-6	0.88
42	2,3-Dihydrobenzofuran	46.32	120	496-16-2	0.15

TABLE 17.3.4. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
43	1,2-Benzenediol (catechol)	47.70	110	120-80-9	<b>15.95</b>
44	1-(5-Methyl-2-furanyl)-1-propanone	48.34	138	10599-69-6	0.55
45	Unknown	49.03	140	N/A	0.46
46	4-Methyl-1,2-benzenediol	49.78	124	452-86-8	0.64
47	1,4-Benzenediol (hydroquinone)	50.43	110	123-31-9	<b>8.36</b>
48	Unknown	50.60	156	N/A	0.84
49	1,3-Benzenediol (resorcinol)	51.11	110	108-46-3	0.78
50	4-Ethylcatechol	51.98	138	1124-39-6	5.48
51	1,1'-Biphenyl-2-ol?	52.66	170	90-43-7	0.15
52	5-Methyl-2-furanmethanol	52.78	112	3857-25-8	0.10
53	2-Phenoxyphenol	52.97	180	10/9/2417	0.54
54	2-Hydroxy-5-methylisophthalaldehyde	53.41	164	7310-95-4	1.26
55	Unknown	53.52	164	N/A	0.99
56	Unknown	55.28	164	N/A	0.46
57	2-Cyclohexene-1,4-diol	56.16	114	41513-32-0	0.44
58	4,4'-Ethylidenediphenol	56.70	214	8/5/2081	0.07
59	7-Hydroxy-2H-1-benzopyran-2-one	56.77	162	93-35-6	0.14
60	4-Hydroxy-9H-xanthen-9-one	58.00	212	14686-63-6	0.05
61	9-Oxabicyclo[3.3.1]nonane-1,4-diol	59.72	158	35377-88-9	0.53
62	2-Dibenzofuranol	60.10	184	86-77-1	0.09
63	4,7-Dimethoxy-2-methyl-1H-indane?	61.16	190	N/A	0.13
64	1,2,3,5-Cyclohexantetraol	61.53	148	53585-08-3	2.73
65	Unknown	62.07	148	N/A	1.38
66	1,1'-Biphenyl-2,3-diol?	63.23	186	1133-63-7	0.11
67	2,5-Dihydroxy-7-oxabicyclo[3.2.1]oct-3-en-6-one	64.30	156	N/A	1.15
68	Unknown	64.74	156	N/A	0.65
69	Unknown	65.33	156	N/A	0.11

Note: Numbers in bold indicate the major pyrolysis constituents.

Similar to the case of quinic acid, it is expected that part of the pyrolysis products of chlorogenic acid will contain compounds with several OH groups (and possibly COOH groups) and will not elute from the chromatographic column in the conditions described in Table 4.6.1. For this reason, chlorogenic acid was pyrolyzed and analyzed off-line after silylation of the pyrolysate to TMS derivatives using BSTFA in DMF (see Table 4.6.2). The time window between 20.0 min and 60.0 min of the resulting chromatogram is shown in Figure 17.3.7, with peak identification given in Table 17.3.5. The first part of the chromatogram from Figure 17.3.7 shows compounds already identified by online pyrolysis and described in Table 17.3.4.

As expected, chlorogenic acid pyrolysate shows many peaks already identified in the quinic acid pyrolysate. Some new compounds were generated from the caffeic acid moiety, and a few fragments contained moieties from both quinic and chlorogenic acid. Some of these fragments elute late in the chromatogram (and are not shown in Figure 17.3.7). Except for the compound eluting at 57.45 min (also not very high) these late eluting components are present only at very low levels. The ester group being

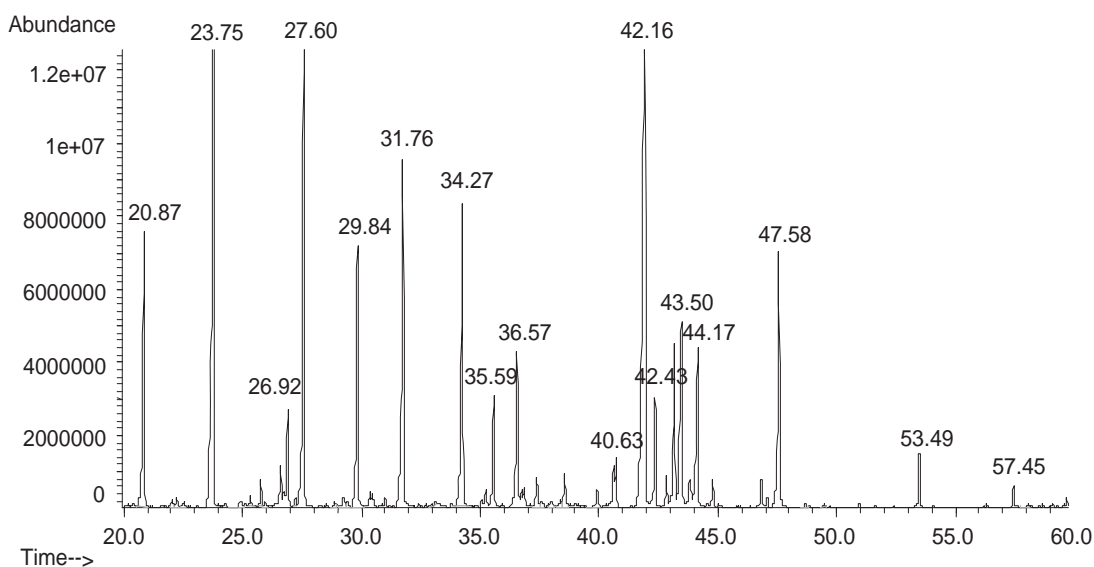


FIGURE 17.3.7. Time window 20–60 min from the chromatogram of silylated pyrolysate of chlorogenic acid at 900°C. Peak assignment is given in Table 17.3.5 based on retention times.

TABLE 17.3.5. Identification of the main peaks in the chromatogram shown in Figure 17.3.7 for the pyrolysate of chlorogenic acid derivatized with bis(trimethylsilyl)trifluoro-acetamide (BSTFA) and their molar level relative to quinic acid  $\gamma$ -lactone 3 TMS

No.	Compound	Ret. time	MW	Fragment ions m/z (intensity)	Mole percent lactone
1	Benzoic acid TMS	20.87	194	179(100), 105(55), 135(43), 77(32), 194(8)	<b>48.54</b>
2	2,6-Dihydroxy-1,4-dioxane 2 TMS	22.56	264	117(100), 73(84), 161(60), 101(50), 191(23)	0.80
3	Catechol 2 TMS	23.75	154	73(100), 254(46), 239(9), 151(8), 255(8)	<b>158.77</b>
4	Unknown	25.79	236	147(100), 73(100), 221(20)	3.37
5	4-Methylcatechol 2 TMS	26.92	268	73(100), 268(55), 253(10)	<b>11.34</b>
6	Hydroquinone 2 TMS	27.60	254	239(100), 254(82), 73(18), 112(10)	<b>58.74</b>
7	Ethyl catechol 2 TMS	29.84	282	73(100), 282(80), 267(22), 179(18), 283(18)	<b>32.64</b>
8	Unknown	30.38	272	156(100), 73(75), 147(30), 257(4), 272(1)	1.91
9	Vinyl catechol 2 TMS	31.76	280	73(100), 280(75), 192(10), 45(10), 265(9)	<b>46.56</b>
10	3-Hydroxybenzoic acid 2 TMS	34.27	282	267(100), 282(45), 223(43), 193(40)	<b>39.82</b>
11	I.S.	35.59	310	310(100), 295(100), 73(45)	<b>12.25</b>
12	4-Hydroxybenzoic acid 2 TMS	36.57	282	267(100), 223(65), 193(55), 282(30)	<b>22.30</b>
13	3,4,5-Trihydroxy-1-cyclohexene-1-carboxylic acid 4 TMS	40.72	462	73(100), 204(96), 147(75), 284(63), 269(38)	3.14
14	Quinic acid $\gamma$ -lactone 3 TMS	42.16	390	73(100), 334(85), 204(72), 256(50), 375(15)	<b>100.00</b>

TABLE 17.3.5. *cont'd*

No.	Compound	Ret. time	MW	Fragment ions m/z (intensity)	Mole percent lactone
15	Quinic acid 1,4-lactone or $\gamma$ -lactone isomer 3 TMS	42.43	390	204(100), 73(92), 334(50), 375(30), 256(18)	9.86
16	1,2,4,5-Tetrahydroxycyclohexane 4 TMS	42.88	436	217(100) 73(25), 375(8), 257(7)	2.61
17	1,3,4,5-Tetrahydroxycyclohexane 4 TMS	43.19	436	217(100) 73(25), 375(23), 257(7)	<b>12.87</b>
18	Unknown	43.44	398	131(100), 73(33), 398(4), 383(4), 295(3)	0.21
19	4,5-Dihydroxy-2-cyclohexenecarboxylic acid 3 TMS	43.50	462	204(100), 73(75), 370(50), 193(48), 462(3)	<b>19.40</b>
20	Unknown	43.83	552	308(100), 73(50), 354(20), 267(20), 251(17)	2.99
21	Unknown	44.10	552	204(100), 73(46), 147(20), 357(6), 462(2)	0.15
22	Isomer quinic acid 5 TMS	44.17	552	73(100), 204(80), 334(75), 129(54), 347(4)	<b>12.61</b>
23	Quinic acid 5 TMS	44.81	552	345(100), 73(47), 255(33), 435(5), 462(2)	1.81
24	Unknown	46.84	552	293(100), 73(83), 308(75), 322(2)	2.01
25	3,4-Dihydroxyhydrocinnamic acid 3 TMS	47.58	398	179(100), 398(90), 73(65), 267(60), 399(33)	<b>22.60</b>
26	3,4-Dihydroxycinnamic acid 3 TMS	53.49	396	396(100), 219(86), 73(73), 397(33)	4.37
27	Fragment with both moieties of chlorogenic acid 3 TMS	57.45	446?	269(100), 446(70), 73(70), 431(20), 241(20)	<b>1.18</b>

Note: Numbers in bold indicate the major pyrolysis constituents.

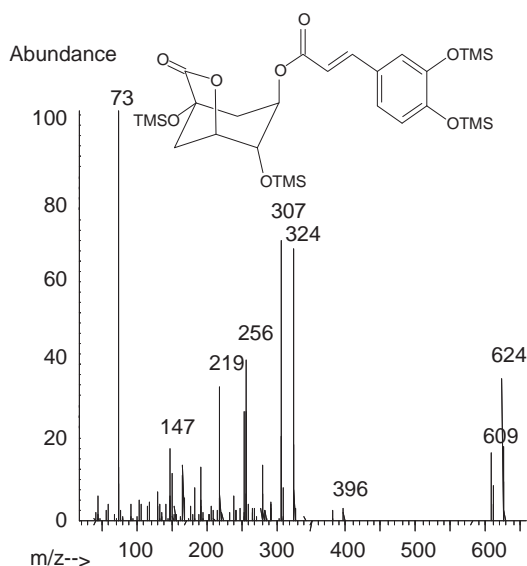


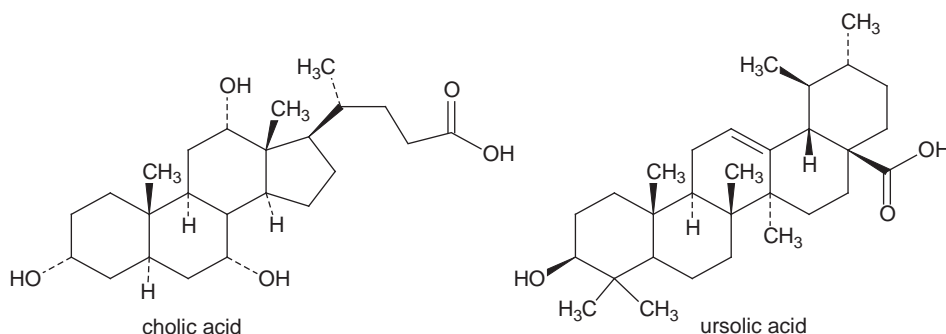
FIGURE 17.3.8. Mass spectrum of TMS derivative of 5-cafeoyl-quinic acid  $\gamma$ -lactone.

easily cleaved, other fragment molecules are generated by reactions already discussed either for caffeic acid or for quinic acid. The spectrum of TMS derivative of 5-caffeoyl-quinic acid  $\gamma$ -lactone is shown in Figure 17.3.8. The retention time of this compound is 75.3 min in the conditions of separation as described in Table 4.6.2.

Chlorogenic acid pyrolysis also forms a relatively large amount of char. Char formation at different temperatures ranging from 250 °C to 750 °C and the structure of the char were reported in the literature [15,46]. The char yield in nonoxidative conditions decreased from 80% at 250 °C to 20% above 550 °C. In oxidative conditions, the char was completely oxidized at 550 °C. The H/C and O/C ratios in the char decreased as the temperature increased. NMR analysis showed that the resonance bands corresponding to CO groups mostly disappeared above 350 °C, and the phenolic groups became almost totally absent at 650 °C in the char. The aromatic character of the char was enhanced with increasing temperature. At 750 °C the char was found to have mainly a graphite-like structure [46].

### Terpenoids with carboxyl and OH groups

A number of natural compounds with terpenoid structure contain both COOH and OH groups. Among these are steroid type acids such as cholic acid and chenodeoxycholic acid (which are produced by the liver and are among the most important bile acids), pentacyclic triterpenoids such as ursolic acid, asiatic acid, madecassic acid (which are present in many plants), etc. The structures of cholic acid and ursolic acid are given below:



The perhydrocyclopentanophenanthrene basic structure in cholic acids and that of eicosahydri-pene in ursolic, asiatic or madecassic acids are stable upon pyrolysis. Pyrolysis of these compounds at temperatures above 700–800 °C generate some of the intact parent molecule, some molecules generated by the elimination of H<sub>2</sub>O from the OH groups, and also numerous small fragment molecules including cyclohexane moieties. Also, aromatic compounds are formed during pyrolysis. The aromatic compounds include alkylbenzenes, naphthalenes, indene and substituted indenenes, anthracene, phenanthrene and substituted phenanthrenes, chrysene, etc. The elimination of H<sub>2</sub>O from the cyclohexane cycle leads to the formation of double bonds, which increases the propensity for PAHs formation. Cholic acid pyrolyzed at 900 °C for 10 s followed by the reaction of the pyrolysate with BSTFA in DMF and GC/MS analysis of the resulting TMS derivatives shows that considerable levels of the parent compound remained intact. The window between 72 min and 77 min from the chromatogram of derivatized cholic acid is given in Figure 17.3.9. The chromatographic conditions for the separation are given in Table 4.6.2. The spectrum of TMS derivative of cholic acid (cholic acid 4 TMS) is given in Figure 17.3.10.

All the peaks shown in the window 72–77 min in the chromatogram from Figure 17.3.9 belong to compounds resulting from two water molecules elimination from the cholic acid (peaks at 72.50, 76.33, and 73.21 min) having MW = 516 for the 2 TMS derivative, or one water molecule elimination (peaks at 72.83, 73.41, 73.67, 74.99, 75.17, and 75.59 min) having MW = 606 for the 3 TMS derivative. The rest of the chromatogram does not contain other major peaks.

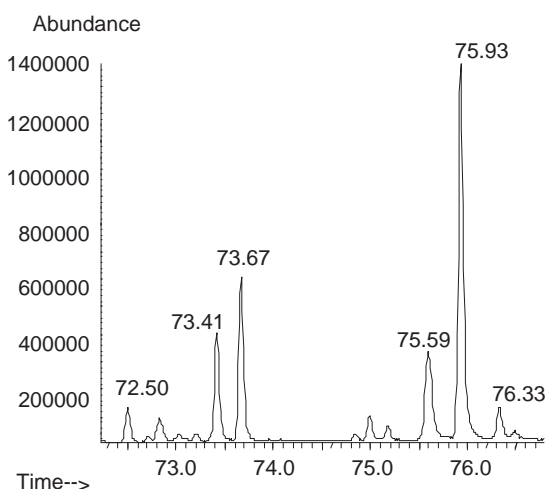


FIGURE 17.3.9. Window from the chromatogram of TMS derivatized pyrolysate of cholic acid.

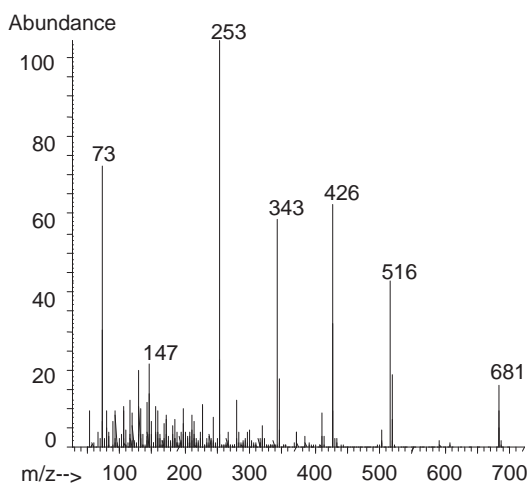


FIGURE 17.3.10. Mass spectrum of cholic acid 4 TMS (MW = 697).

## 17.4. CARBOXYLIC ACIDS WITH OTHER ADDITIONAL FUNCTIONALITIES OR GROUPS

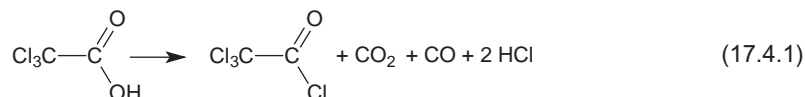
### General aspects

Besides OH and  $\text{NH}_2$ , other functional groups can be present in an acid molecule. These include halogen, carbonyl, and other less common functional groups (e.g., thiol, sulfone, nitrile, etc.). The presence of these groups can influence pyrolysis results not only as independent functionalities, but also interacting with the COOH group, as it was described in some cases for OH groups. Acids with additional functionalities such as Cl are typically synthetic compounds, while acids containing carbonyl groups, such as pyruvic acid, acetoacetic acid, and levulinic acid, are common in nature.

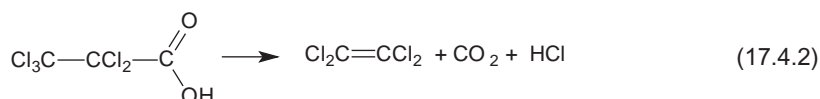
### Halogeno acids

Similar to other additional functional groups, the halogen can be present in  $\alpha$ ,  $\beta$ ,  $\gamma$ , etc. position relative to the COOH group. Monochloroacetic acid decomposes differently from acetic acid, generating a

mixture of pyrolysis products containing CO, CO<sub>2</sub>, HCl, HCHO, and low levels of halogenated hydrocarbons. Trichloroacetic acid at 300 °C and decomposition times around 4 h reacts as follows:

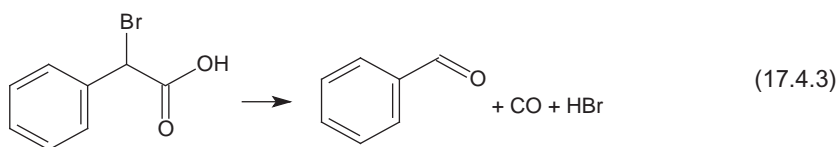


The formation of CHCl<sub>3</sub> was not noticed in this pyrolysis process. As seen from reaction 17.4.1, the elimination of HCl from the acid involves the hydrogen from the carboxyl group. The same effect is seen in pyrolysis of pentachloropropionic acid:



The high stability of HCl at elevated temperatures, as well as its relatively high (absolute) value of the heat of formation, favors the elimination of HCl during pyrolysis.

Substitution of a Br atom on the α-position in phenylacetic acid also affects the pyrolysis result. α-Bromophenylacetic acid in the range 260–315 °C at pressures between 20 Torr and 70 Torr, and in the presence of toluene as a free radical inhibitor, undergoes pyrolysis as follows:

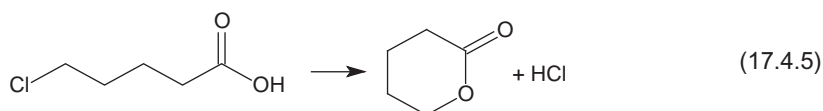


This reaction was found to be unimolecular with a first-order rate and to follow Arrhenius equation:

$$\log_{10} k \text{ (s}^{-1}\text{)} = (12.23 \pm 0.26) - \frac{(164.9 \pm 2.7) \text{ kJ/mol}}{2.303 RT} \quad (17.4.4)$$

Small amounts of CO<sub>2</sub> and benzyl bromide were also generated in reaction 17.4.3 [41].

When the halogen atom is attached in γ or δ positions, and the formation of lactones is possible, the first steps during thermal degradation of halogenated acids is the formation of lactones by the elimination of the hydrohalogenated acid. The reaction is shown below for δ-chlorovaleric acid (5-chloropentanoic acid), which generates δ-valerolactone (tetrahydro-2H-pyran-2-one):



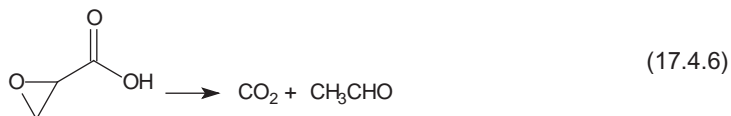
In a similar reaction, γ-bromocaproic acid (4-bromohexanoic acid) generates 5-ethylidihydro-2(3H)-furanone (5-ethylbutyrolactone).

Molecules containing various functional groups, such as COOH, OH, and Cl may undergo more complex reactions. For example, 1-chloro-2-hydroxy-1-methylethane-1,2-dicarboxylic acid generates by thermal degradation CO<sub>2</sub>, HCl, and propionaldehyde [49].

### Cyclic ether acids

Carboxyl group can be attached to an epoxide or a cyclic ether. Epoxides are not very stable compounds, and the expected decarboxylation reaction is typically associated with the opening of the

oxirane ring. For example, oxirane-2-carboxylic acid (glycidyl carboxylic acid) decomposes as shown below:

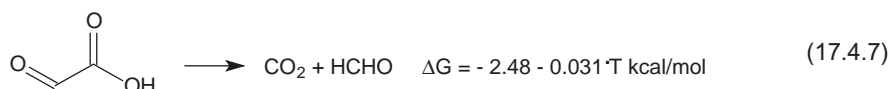


A similar reaction is noticed for the compounds with different substituents at the oxirane ring. The acids with the carboxyl group substituted at stable cyclic ether rings typically decompose with decarboxylation. A similar reaction with  $\text{CO}_2$  elimination and opening of the oxirane ring takes place during the pyrolysis of 2-methyloxirane-2,3-dicarboxylic acid (oxycitraconic acid), which generates propionaldehyde and  $\text{CO}_2$ . Typical for dicarboxylic acids with the  $\text{COOH}$  group on a heterocyclic ring, the formation of anhydrides by water elimination is not favored.

### Aldehyde acids and keto acids

Aldehyde acids and keto acids include compounds such as glyoxylic acid (oxoacetic acid), pyruvic acid, and levulinic acid (4-oxopentanoic acid). Similar to the situation of other compounds with more functional groups, the second group can be in  $\alpha$ ,  $\beta$ ,  $\gamma$ , etc. position to the carboxyl. Aldehyde and keto acids also include more complex compounds, some resulting from the oxidation of sugars. The sugar acids from this group contain the OH functionality besides carboxyl and carbonyl, and include uronic acids and ketoaldonic acids. Pyrolysis of a uronic acid (glucuronic acid) was described in Section 16.3.

Glyoxylic acid is the simplest  $\alpha$ -carbonyl organic acid. At temperatures above  $100^\circ\text{C}$ , thermal decomposition of glyoxylic acid monohydrate in a sealed tube generates oxalic acid and glycolic acid, due to a Cannizzaro type reaction of the aldehyde group (see reaction 2.5.1). During thermal decomposition in a static system in the temperature range  $200\text{--}537^\circ\text{C}$  and pressures between 0.4 Torr and 8 Torr, the main pyrolysis products were  $\text{CO}_2$  and  $\text{HCHO}$  [50].

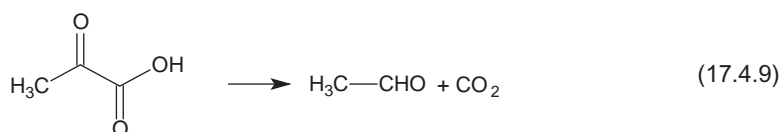


First-order rate constant for the formation of  $\text{CO}_2$  in reaction 17.4.7 is given by the expression:

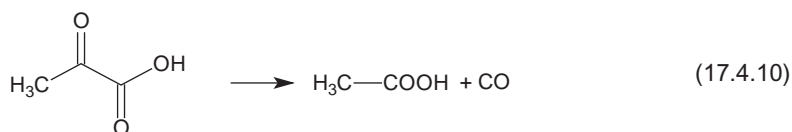
$$\log_{10} k \text{ (s}^{-1}\text{)} = 7.80 - \frac{30.8 \text{ kcal/mol}}{2.303 RT} \quad (17.4.8)$$

Besides carbon dioxide and formaldehyde, low levels of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$  (CO less than 10% of  $\text{CO}_2$  level) are also formed during glyoxylic acid thermal decomposition, and the ratio  $\text{CO}/\text{CO}_2$  increases as the temperature increases. The levels of  $\text{HCHO}$  in the pyrolysate were somewhat lower than those of  $\text{CO}_2$ , which indicates either some decomposition of  $\text{HCHO}$  formed in reaction 17.4.7 or the formation of  $\text{CO}_2$  by other mechanisms. The decomposition of glyoxylic acid induced by a pulsed laser with estimated temperatures between 1100 K and 1600 K showed the same behavior as the static system [50]. It is likely that the formation of  $\text{CO}$  and  $\text{H}_2$  is a result of  $\text{CO}$  elimination with  $\text{HCOOH}$  formation, the formic acid being further decomposed into  $\text{CO}$  and  $\text{H}_2\text{O}$ .

Pyruvic acid (2-oxopropanoic acid) is an  $\alpha$ -keto acid, which can be considered derived from glyoxylic acid with a  $\text{CH}_3$  substituent to the hydrogen atom bound to the CO group. During pyrolysis this compound generates mainly  $\text{CO}_2$  and acetaldehyde. The formation of acetic acid and  $\text{CO}$  also takes place, but to a lower extent. The two reactions are shown below:





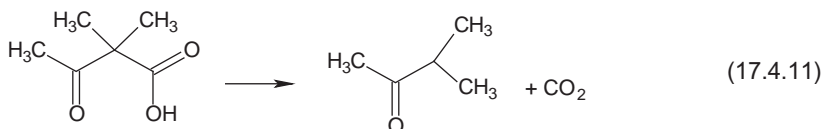


Pyrolysis of pyruvic acid also leads to the formation of some condensation products.

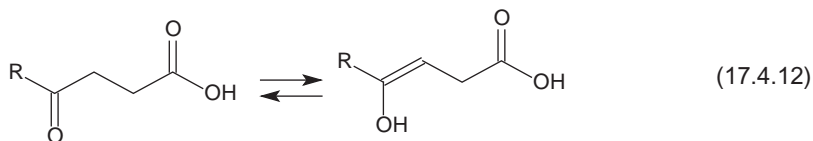
Similar to pyruvic acid, phenylglyoxylic acid (phenyl substituted to glyoxylic acid) decomposes above 300 °C with the formation of CO<sub>2</sub>, CO, benzaldehyde, and benzoic acid.

Particular substituents to glyoxylic acid may influence the pyrolysis outcome. Thienyl group, for example, leads to the generation of CO<sub>2</sub> exclusively and the formation of thiophene-2-carboxaldehyde (in addition to some charring).

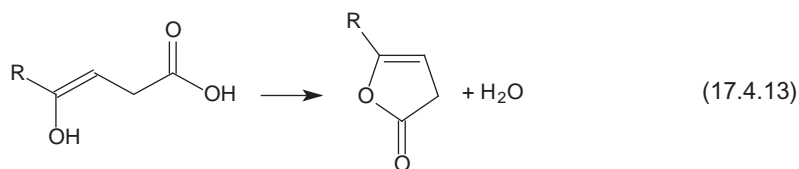
Pyrolysis of β-ketonic acids typically leads to the elimination of CO<sub>2</sub> and the formation of a ketone. Ketones are in general relatively stable to heating, and if a carboxyl group is attached to the same molecule, the decarboxylation process usually takes place before the ketone decomposition. Acetoacetic acid (3-oxobutanoic acid), for example, is not very stable and decomposes into CO<sub>2</sub> and acetone below 100 °C. Similarly, 2,2-dimethyl-3-oxobutanoic acid generates CO<sub>2</sub> and methylisopropyl ketone.



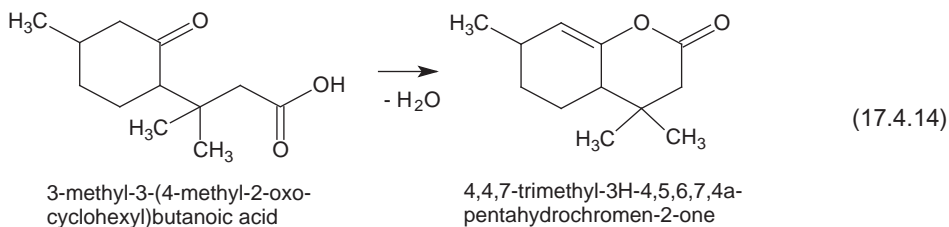
γ-Ketonic acids and δ-ketonic acids behave differently from α- and β-ketonic acids. The keto-enol equilibrium of these compounds allows them to exist (in part) in two forms, as shown below:



The enol form has the capability to generate lactones by water elimination in the first stages of pyrolysis. The process can be written as follows:



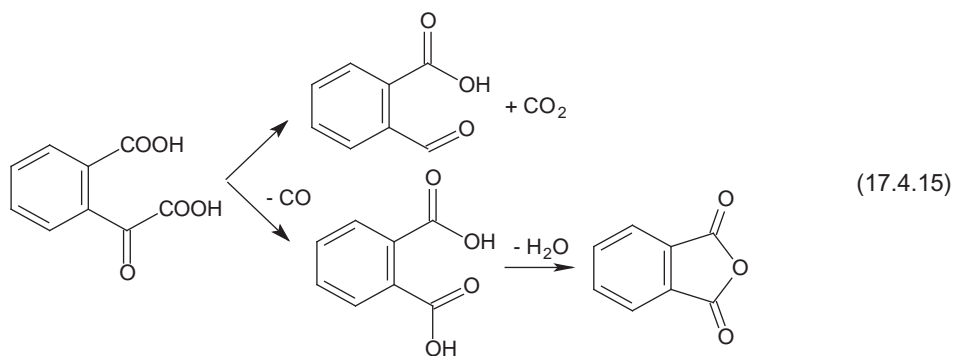
Formation of furanones is characteristic for levulinic acid (4-oxopentanoic acid) as well as for several other similar acids like 2-methyl-4-oxopentanoic acid, 2-ethyl-4-oxopentanoic acid, and 3-methyl-4-oxopentanoic acid. In reactions similar to 17.4.13, δ-ketonic acids generate pyranones. Cyclic lactones are formed even when the carbonyl group is part of a cycloalkane, as shown below for 3-methyl-3-(4-methyl-2-oxo-cyclohexyl)butanoic acid:



If the formation from the ketone of an enol is not possible (e.g., a double bond exists in the β-position to the carbonyl), the decomposition of the keto acids takes place with simple decarboxylation. Some

substituents such as CN positioned between the CO group and the COOH group were found to influence the pyrolysis results and favor decarboxylation [51].

Ketodicarboxylic acids behave similarly with monocarboxylic keto acids. For example, *o*-carboxyphenylglyoxylic acid or 2-(carboxycarbonyl)benzoic acid by thermal decomposition around 180 °C generates both *o*-carboxybenzaldehyde by CO<sub>2</sub> elimination and phthalic anhydride by elimination of CO and then of H<sub>2</sub>O from the intermediate phthalic acid. The reactions are shown below:



Ketoglutaric acid (1-oxopropane-1,3-dicarboxylic acid) decomposes to generate several fragments including propenal, furanone, and dihydro-2,5-furandione. In Figure 17.4.1 is shown the pyrogram of 1 mg ketoglutaric acid performed in a Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900$  °C,  $\beta = 10$  °C/ms, THT = 10 s, and housing temperature  $T_{hou} = 280$  °C, with the pyrolysate analyzed under conditions given in Table 4.6.1. The compound identifications obtained based on their mass spectra and their relative molar content in 100 moles of pyrolysate based on peak areas are given in Table 17.4.1.

The formation of butanoic acid lactone or 2(3H)-furanone is a result of elimination of one CO<sub>2</sub> and one H<sub>2</sub>O molecules, with the reaction as shown below:

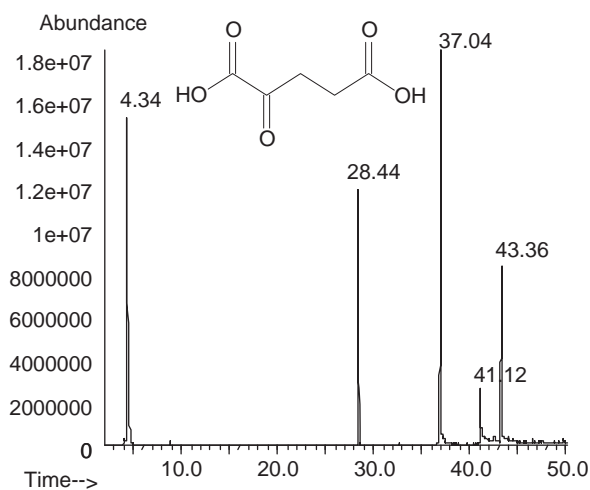
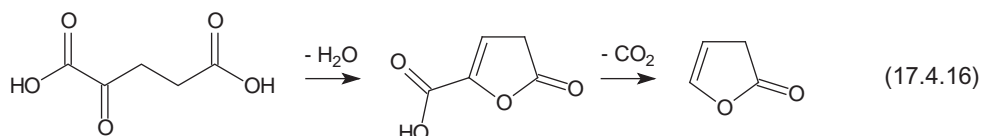


FIGURE 17.4.1. Pyrogram of ketoglutaric acid at 900 °C.

TABLE 17.4.1. Identification of the main peaks in the chromatogram shown in Figure 17.4.1 for the pyrolysis of ketoglutaric acid at 900 °C (hydrogen, methane, ethylene, and water were not analyzed due to the mass spectrometer settings)

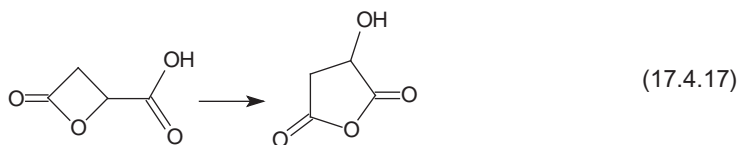
No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Carbon dioxide	4.34	44	124-38-9	<b>40.68</b>
2	Propenal	8.81	56	107-02-8	Trace
3	2(5H)-Furanone	28.44	84	497-23-4	11.24
4	Butanoic acid lactone or 2(3H)-furanone	37.04	84	20825-71-2	<b>31.43</b>
5	Propionic acid	41.13	74	79-09-4	3.83
6	3-Ethyl-4-methyl-2,5-furandione	42.53	140	3552-33-8	Trace
7	Dihydro-2,5-furandione	43.36	100	108-30-5	12.83
8	5-Ethylcyclopent-1-ene-carboxaldehyde	46.47	124	36431-60-4	Trace

Note: Numbers in bold indicate the major pyrolysis constituents.

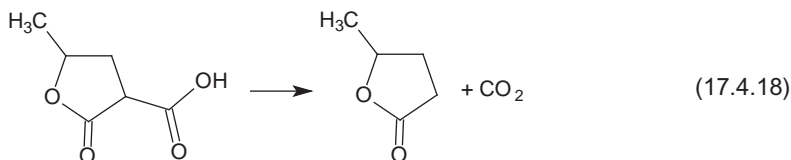
The formation of 2(5H)-furanone is probably the result of a migration of the double bond in the butanoic acid lactone. Dihydro-2,5-furandione formation is a result of H<sub>2</sub>O and CO eliminations. The formation of propenal is the result of a double decarboxylation. Traces of higher molecular weight compounds are the result of condensation reactions.

### Lactonic acids

Dicarboxylic acids that also contain an OH group in the molecule can form lactones involving one of the COOH groups. For example, a  $\beta$ -lactone can be formed from malic acid (hydroxybutanedioic acid). This compound decomposes as shown in the following reaction:



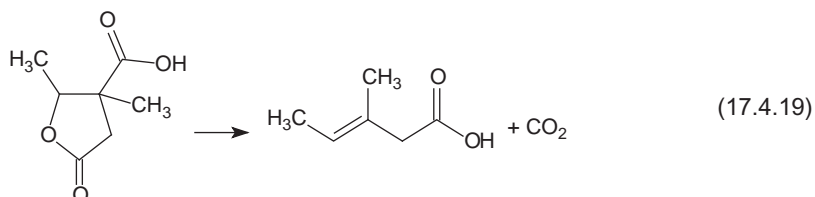
The four-atom cycle tension and the stability of the tetrahydrofuranone cycle easily explain this reaction path. Thermal decomposition of  $\gamma$ -valerolactone carboxylic acid simply generates CO<sub>2</sub> and forms  $\gamma$ -valerolactone, which is also a stable compound. The reaction is shown below:



These reactions show that the decarboxylation takes place much more easily in comparison with the decomposition of trihydrofuranone cycle. Other acids with the COOH group attached in 3-position in the furanone cycle also decompose with decarboxylation [13].

Some lactonic acids eliminate CO<sub>2</sub>, but the reaction takes place with the opening of the lactone ring and the formation of an unsaturated acid, as shown below for  $\beta,\gamma$ -dimethyl-paraconic

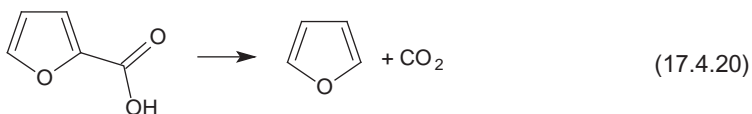
acid (2,3-dimethyl-5-oxo-2,3,4-trihydrofuran-3-carboxylic acid):



However  $\alpha$ -ethyl- $\gamma$ -methylparaconic acid generates both diethylmaleic anhydride and  $\alpha$ -ethyl- $\gamma$ -methylpentenoic acid.

### Acids with the carboxyl group attached to an aromatic heterocycle

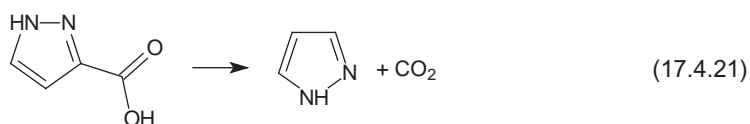
Carboxyl groups are found in many compounds connected to an aromatic heterocyclic structure. Thermal decomposition of these acids usually takes place with decarboxylation and the formation of the heterocyclic compound. Pyrolysis of heterocyclic compounds is discussed in Chapter 21, but heterocyclic acids are included in this chapter since their pyrolysis typically does not affect the stable heterocycle moiety. For example, 2-furancarboxylic acid (furoic acid) starts decomposing around 220 °C by the following reaction:



For the case of a double unsaturated six-atom cycle containing one oxygen atom, neither  $\alpha$ -pyran nor  $\gamma$ -pyran have an aromatic character, and these compounds are not stable (see Chapter 21). However by pyrolysis,  $\gamma$ -pyrone is generated from 4-oxo-4H-pyran-2-carboxylic acid (comanic acid), and both  $\gamma$ -pyrone and comanic acid together with some char are generated from 4-oxo-4H-pyran-2,6-dicarboxylic acid (chelidonic acid). Chromone carboxylic acid also suffers decarboxylation upon heating to generate chromone.

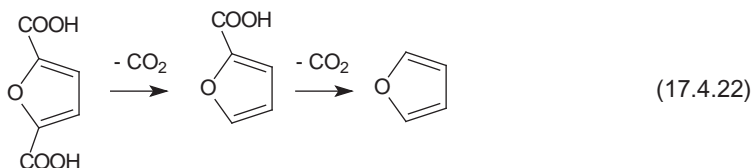
Carboxylic acids having the carboxyl group attached to stable aromatic heterocycles containing nitrogen behave similarly to the acids having the carboxylic group connected to an oxygen-containing stable heterocycle. For example, 2-pyrrole carboxylic acid decomposes around 190 °C to generate pyrrole and CO<sub>2</sub>. Similar reactions take place for many 2-pyrrole carboxylic acids with various substituents at the pyrrole ring. Indole carboxylic acids and their ring-substituted derivatives behave similarly to pyrrole-2-carboxylic acid.

Monocarboxylic acids derived from pyridine (pyridine-2-carboxylic acid or  $\alpha$ -picolinic acid, pyridine-3-carboxylic acid or nicotinic acid, and pyridine-4-carboxylic acid or isonicotinic acid) are relatively stable up to 250–260 °C. Above this temperature and depending on the heating time, the main decomposition reaction is decarboxylation.  $\alpha$ -Picolinic acid and isonicotinic acid seem to decompose at a slightly lower temperature compared to nicotinic acid. Similarly, quinoline-2-carboxylic acid (quinaldinic acid) generates by pyrolysis quinoline, acridine-10-carboxylic acid generates acridine, etc. A carboxyl group substituted on a pyrazole ring in 2, 3, or 4 positions behaves similarly to other cases of stable heterocyclic acids generating pyrazole and CO<sub>2</sub> when heated around the melting point of each acid. The reaction for pyrazole-3-carboxylic acid is shown below:



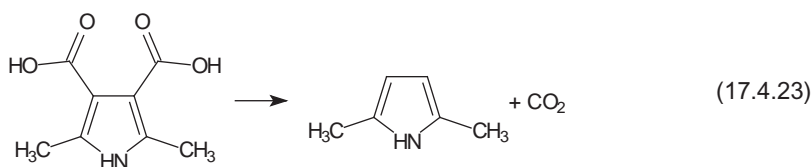
The decarboxylation reaction is also characteristic for thiazoles, triazoles, pyridazines, and other stable heterocyclic compounds, with or without additional substituents at the heterocyclic ring [13].

Thermal decomposition of di- and tri-carboxylic acids with COOH groups on stable heterocyclic rings typically occur with a decarboxylation reaction, leading either to the monocarboxylic acid or directly to the stable heterocycle. For example, furan-2,5-dicarboxylic acid decomposes with the formation of both furan and furoic acid as shown in the reaction below:



The decarboxylation reaction in this case can be attributed to the steric unfavorable position of the carboxyl groups. Other compounds derived from furoic acid with different substituents at the furan ring, decompose similarly to furoic acid derivative. Pyrrole-2,5-dicarboxylic acid generates pyrrole but also char. Pyridine dicarboxylic acids also decompose with CO<sub>2</sub> elimination, and in the first step generate pyridine monocarboxylic acids. Quinolinic acid (pyridin-2,3-dicarboxylic acid) generates preferentially nicotinic acid, while cincomeronic acid (pyridin-3,4-dicarboxylic acid) generates a mixture of nicotinic and isonicotinic acids.

In the case of heterocyclic carboxylic acids with the COOH groups in vicinal positions on the ring, thermal decomposition takes place differently from that of homocyclic compounds. It was shown, for example, that phthalic acid and several benzene ring-substituted phthalic acids generate by pyrolysis the corresponding phthalic anhydride by water elimination (see reaction 17.2.18). In the case of vicinal COOH groups substituted on heterocyclic rings, the main reaction is still decarboxylation. As an example, thermal decomposition of 2,5-dimethylpyrrole-3,4-dicarboxylic acid generates 2,5-dimethylpyrrole and CO<sub>2</sub> as shown in the reaction below:

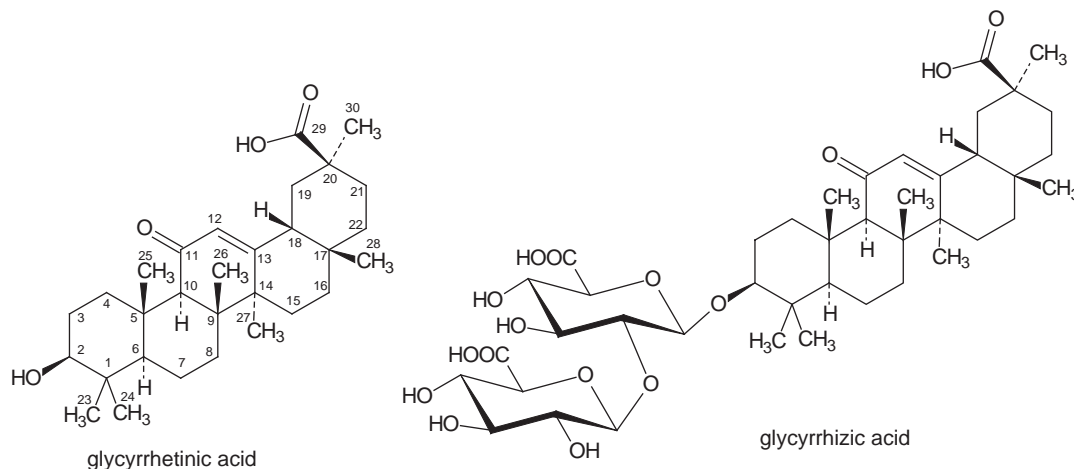


Decarboxylation is the main process taking place in carboxylic acids with the COOH groups on a pyridine ring or furan ring.

### Terpenoids with carboxyl and carbonyl groups

A number of natural terpenoids contains in their molecule carboxyl and carbonyl groups. These compounds are relatively stable to pyrolysis, and besides CO<sub>2</sub> elimination that takes place from the carboxyl group, the pyrolysis at temperatures above 650–700 °C leads to a multitude of fragments. Many of these fragments contain one or more cyclohexane cycles with various substituents and various degrees of unsaturation. The complexity of pyrolysis products typically depends on the whole molecular structure more than on attached functionalities. Two examples of compounds from this class are discussed below. One is glycyrrhetic acid, a pentacyclic triterpenoid related to β-amyrin and containing a dodecahydronicene skeleton. Glycyrrhetic acid is present in nature mainly in the form of glycyrrhizic acid, a saponin glycoside with two connected glucuronic acid molecules. Glycyrrhizic acid is typically found in licorice root in the form of Ca<sup>2+</sup> or K<sup>+</sup> salts, and it is used as a sweetener in the form

of its  $\text{NH}_4^+$  salt. The formulas of the two compounds are given below:



The pyrograms generated from 1 mg glycyrrhetic acid and 1 mg glycyrrhizic acid mono ammonium salt generated in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ , are given in Figure 17.4.2 A and B. The reference signal (for glycyrrhetic acid trace B) is inverted vs. the signal for glycyrrhizic acid (trace A). Both traces are very complex, that of glycyrrhizic acid containing virtually all the peaks also present in the trace of glycyrrhetic acid. The pyrograms were obtained using conditions given in Table 4.6.1.

Both pyrograms contain  $\text{CO}_2$  (eluting at 4.24 min), isoprene (eluting at 7.38 min), and many fragments containing cyclohexane cycles with different substitutions and different degrees of unsaturation. In contrast to glycyrrhetic acid, the pyrogram of glycyrrhizic acid contains more aromatic compounds. For example, the peak at 16.61 min belongs to benzene, that at 23.11 min belongs to toluene, that at 28.27 min to *m*-xylene, the peak at 45.36 min to 2-methylnaphthalene, and the peak at 52.39 min to 1,4,6-trimethylnaphthalene. Other aromatic compounds such as indene, naphthalene, other substituted

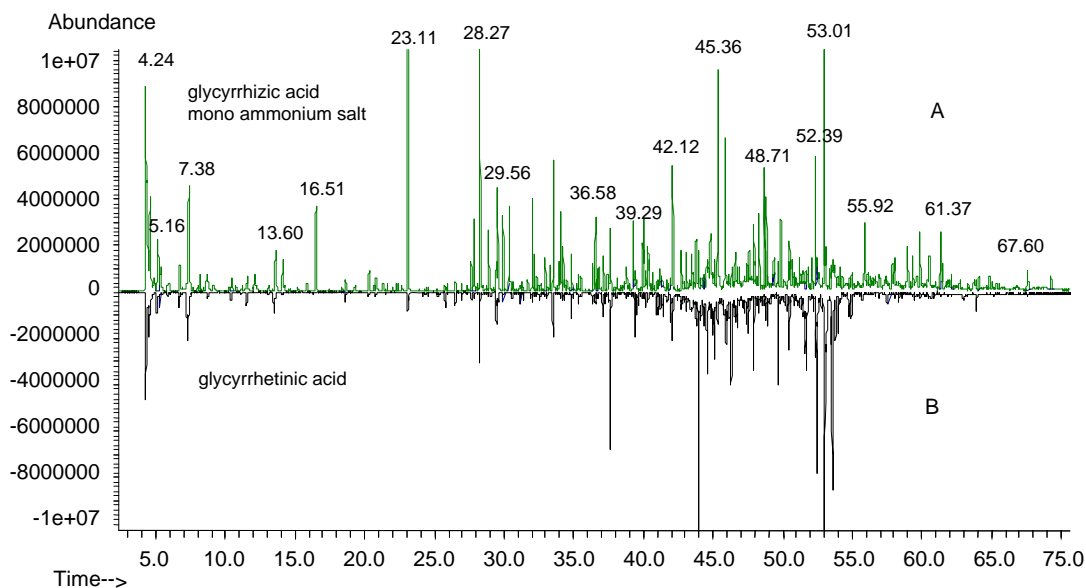


FIGURE 17.4.2. Pyrogram of glycyrrhizic acid (trace A) and of glycyrrhetic acid (trace B) at  $900^\circ\text{C}$ . Trace B is inverted.

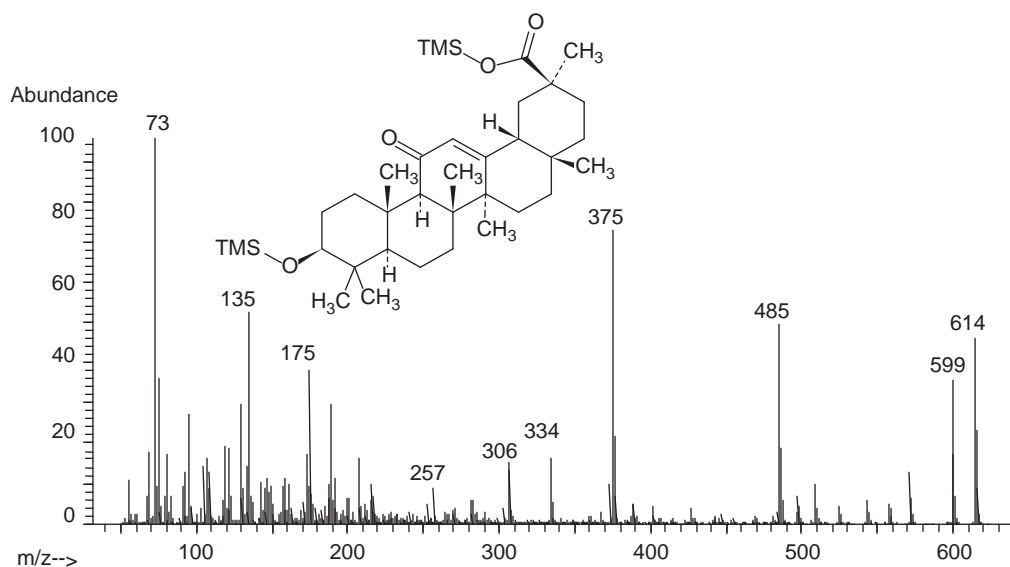


FIGURE 17.4.3. Mass spectrum of glycyrrhetic acid 2 TMS.

naphthalenes, as well as phenanthrene and lower levels of anthracene were detected in the pyrogram A of glycyrrhizic acid, but were virtually absent in pyrogram B of glycyrrhetic acid. The transfer of glycyrrhetic acid into its pyrolysate and particularly into the pyrolysate of glycyrrhizic acid is of special interest. Glycyrrhizic acid can be used as licorice flavorant in different consumer products including cigarettes, and the formation of glycyrrhetic acid during pyrolysis is of concern since this compound is biologically active (see, e.g., [52]). In the pyrolysates of both glycyrrhetic acid and glycyrrhizic acid generated at temperatures as high as 900 °C, low levels of glycyrrhetic acid were detected. The compound does not elute in the conditions given in Table 4.6.1 on a more polar DB-1701 chromatographic column, and the identification is possible only by off-line pyrolysis followed by the silylation of the pyrolysate and analysis under conditions given in Table 4.6.2. The spectrum of glycyrrhetic acid 2 TMS (eluting at 89.5 min in the conditions described in Table 4.6.2) is given in Figure 17.4.3. Traces of a fragment molecule generated by the elimination of the OH group from the 2 position of glycyrrhetic acid were also detected in both pyrolysates, but the decarboxylated form of the acid was not detected in the pyrolysate.

## 17.5. SALTS OF CARBOXYLIC ACIDS

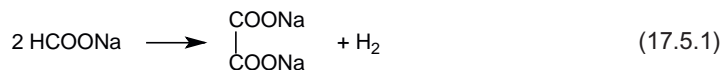
### General aspects

Pyrolysis of carboxylic acid salts is a complex subject since it is affected by many parameters, which include the nature of the acid, the nature of the metal, and the pyrolysis conditions. For the case of organic salts, the results of pyrolysis are frequently specific for a particular molecular structure [13,53,54]. This is in contrast with other classes of compounds where selected examples were also discussed, but they were usually representative for the family of compounds.

Pyrolysis of organic acid salts has been utilized in organic synthesis as well as for the preparation of specific inorganic combinations such as oxides or even metals [55] or superconducting materials [56].

### Salts of short chain aliphatic acids

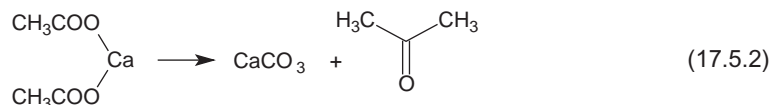
Sodium formate generates by pyrolysis around 450 °C sodium oxalate by the following reaction:



The reaction is associated with the formation of other compounds including HCHO, CH<sub>3</sub>OH, CO, Na<sub>2</sub>CO<sub>3</sub>, and HCOOCH<sub>3</sub>. A basic medium (1% NaOH) increases the yield of oxalate. Pyrolysis of calcium formate does not generate more than traces of calcium oxalate and decomposes with the formation of CO, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and traces of other short chain hydrocarbons. Formiates of other metals generate different products. For example, barium formate pyrolyzed around 400 °C generates CO, CO<sub>2</sub>, H<sub>2</sub>, and low levels of CH<sub>3</sub>OH, and Sn<sup>+2</sup> formate generates a larger yield of HCOOCH<sub>3</sub>.

Sodium acetate is relatively stable to heating. At temperatures around 400 °C, it generates mainly CH<sub>4</sub>, CO<sub>2</sub>, Na<sub>2</sub>O, and C [57].

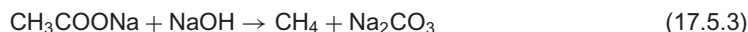
In contrast, calcium acetate pyrolyzes following the reaction:



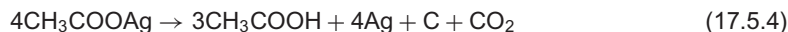
The formation of carbonyl compounds is also noticed for other acids and for other alkaline earth metals (e.g., Ba<sup>+2</sup>). For example, calcium butyrate generates by pyrolysis at 300–400 °C dipropyl ketone, and calcium phenylacetate generates 1,3-diphenylacetone. However, pyrolysis of many calcium salts (and of other alkaline earth metals) does not have always as a unique result the expected ketone. For example, calcium isobutyrate generates a mixture of diisopropyl ketone (as expected) but also isobutyraldehyde, methyl isopropyl ketone, and other molecular species.

A mixture of calcium salts from different acids can lead to ketones with different radical substituents to the carbonyl group [58]. If one of the components in the mixture is calcium formate, the results are aldehydes. As a general case, (R–COO)<sub>2</sub>Ca mixed with (HCOO)<sub>2</sub>Ca generates by pyrolysis the R–CHO aldehyde.

Pyrolysis of salts of organic acids in the presence of a strong base, typically generates hydrocarbons. The reaction is shown below for sodium acetate, but the reaction takes place in a similar way for other organic acids:



The salts of some relatively inert metals such as Ag, Cu, Hg, Bi, etc. behave differently from the salts of alkaline or alkaline earth metals. Typical for thermal decomposition of these metal salts with organic acids is the formation of the free metal, CO<sub>2</sub>, carbon and the free acid, as shown in the following reaction for the silver salt of acetic acid:

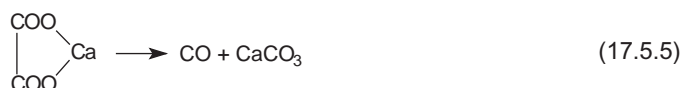


Variations of reaction 17.5.4 are seen for other acids with relatively inert metals. For example, bismuth subgallate, C<sub>6</sub>H<sub>2</sub>(OH)<sub>3</sub>COOBiO, by heating at around 300 °C generates metallic Bi and various decomposition products of gallic acid [24].

The formation of carbon and metals from some salts decomposition has been used to produce metallic nanoparticles encapsulated in polyhedral graphite cages, for example for nickel stearate [59].

Pyrolysis of the salts of dicarboxylic acids does not involve different reactions compared to that of monocarboxylic acids [60]. Sodium oxalate, for example, is relatively stable to thermal decomposition up to 350–400 °C. Higher temperatures or extended heating time generates carbon, CO, CO<sub>2</sub>, and Na<sub>2</sub>CO<sub>3</sub>. Calcium oxalate decomposes similarly, and the thermogram of a Ca(OOC)<sub>2</sub> H<sub>2</sub>O sample is shown in Figure 17.5.1.

The initial process is the elimination of H<sub>2</sub>O. At temperatures around 450 °C, the following reaction takes place:





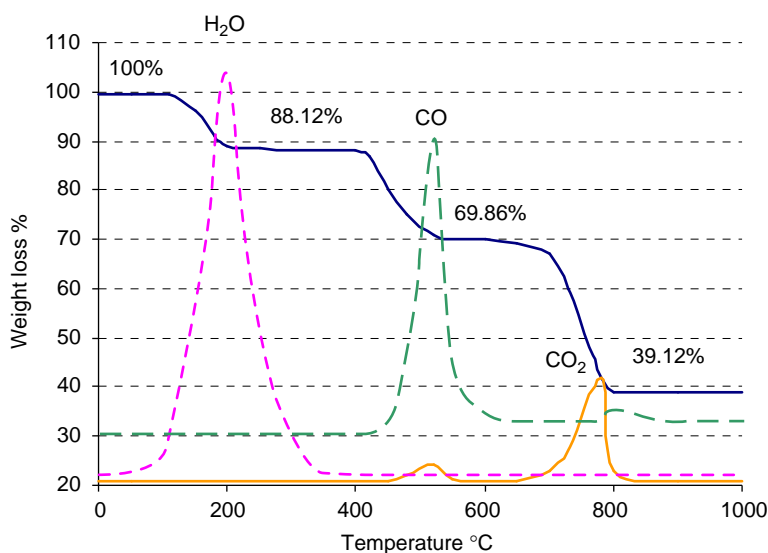


FIGURE 17.5.1. Thermogram of  $\text{Ca}(\text{OOC})_2 \cdot \text{H}_2\text{O}$  also showing the evolution of gases.

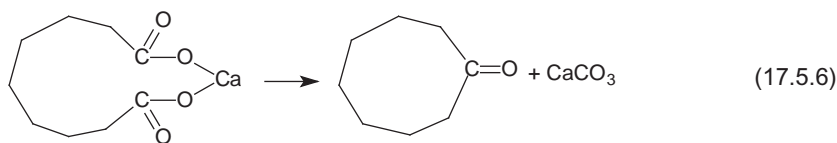
At higher temperatures around  $780^\circ\text{C}$ , the calcium carbonate starts decomposing to form  $\text{CO}_2$  and  $\text{CaO}$ . As seen from Figure 17.5.1, a small amount of  $\text{CO}_2$  also is formed at the same temperature where  $\text{CO}$  is generated.

Pyrolysis of oxalates of more inert metals such as  $\text{Fe}$  generates  $\text{CO}$ ,  $\text{CO}_2$ , and a mixture of metal and metal oxides [61].

### Other organic acids salts

The salts of the acids containing a long aliphatic chain are known as soaps. Soaps pyrolysis is of interest mainly since special soaps are frequently used in the manufacturing of various plastics as slip agents (particularly  $\text{Ca}^{+2}$  and  $\text{Zn}^{+2}$  salts). The slip agents are used to avoid sticking of the polymer to the processing machines that work at temperatures of  $200\text{--}300^\circ\text{C}$ . Pyrolysis of soaps typically generates hydrocarbons. Sodium stearate at  $300\text{--}350^\circ\text{C}$  generates a mixture of decane, decene, tetradecane, pentadecane, etc. Calcium stearate also generates a mixture of hydrocarbons, but containing a considerable proportion of the corresponding ketone. Zinc stearate, a common slip agent, also generates by pyrolysis mainly hydrocarbons [62].

The formation of ketones upon thermal decomposition of calcium salts is also seen for several dicarboxylic acids. For example, calcium succinate forms low levels of cyclohexanedione, and calcium phthalate forms some anthraquinone. Some larger cyclic ketones were obtained from the pyrolysis of calcium salts of  $\alpha,\omega$ -diacids with longer carbon chain, as shown below for calcium salt of heptane-1,7-dicarboxylic acid (azelaic acid):



The results of pyrolysis for the salts of various acids depends considerably on the structure of the acid (besides the existence of a  $\text{COOH}$  group in the molecule) and also on the pyrolysis conditions. As an example, pyrolysis of 1.5 mg of (2*E*,4*E*)-hexa-2,4-dienoic acid potassium salt is shown in Figure 17.5.2. The pyrolysis was performed in a Type 1 Experiment as described in Section 4.6, at

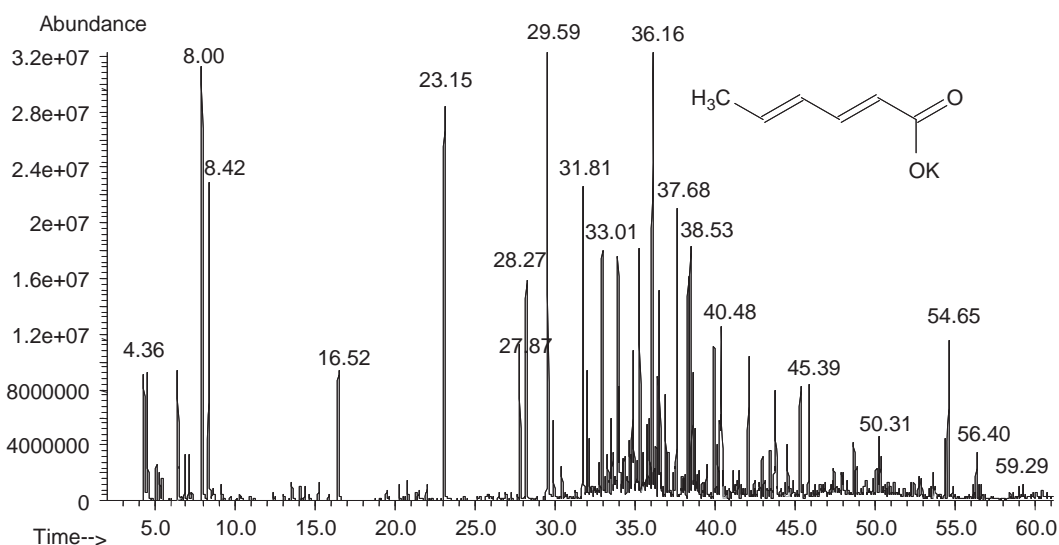


FIGURE 17.5.2. Pyrogram of (2E,4E)-hexa-2,4-dienoic acid potassium salt at 900°C. Peak assignment is given in Table 17.5.1 based on retention times.

TABLE 17.5.1. Identification of the main peaks in the chromatogram shown in Figure 17.5.2 for the pyrolysis of (2E,4E)-hexa-2,4-dienoic acid potassium salt at 900°C (hydrogen, methane, ethylene, water were not analyzed due to the mass spectrometer settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
1	Carbon dioxide	4.36	44	124-38-9	6.17
2	Propene	4.57	42	115-07-1	3.74
3	2-Methylpropene	5.14	56	115-11-7	0.79
4	1,3-Butadiene	5.34	54	106-99-0	0.82
5	2-Butene	5.51	56	590-18-1	0.45
6	1,4-Pentadiene	6.50	68	591-93-5	1.98
7	2-Pentene	6.92	70	646-04-8	0.72
8	1,2-Dimethylcyclopropane	7.17	70	930-18-7	0.64
9	Ethylidenecyclopropane?	8.00	68	18631-83-9	6.68
10	1,3-Pentadiene	8.42	68	504-60-9	4.95
11	Acetone	9.20	58	67-64-1	0.45
12	5-Methyl-1,3-cyclopentadiene	13.61	80	96-38-8	0.46
13	2,4-Hexadiene	15.30	82	6108-61-8	0.31
14	Benzene	16.52	78	71-43-2	2.42
15	2-Methyl-1,3,5-hexatriene?	20.33	94	19264-50-7	0.22
16	5,5-Dimethyl-1,3-cyclopentadiene	20.84	94	4125-18-2	0.34
17	1-Methyl-1,4-cyclohexadiene	22.04	94	4313-57-9	0.16
18	Toluene	23.15	92	108-88-3	6.41
19	Ethylbenzene	27.87	106	100-41-4	1.47
20	1,4-Dimethylbenzene ( <i>p</i> -xylene)	28.27	106	106-42-3	2.37
21	1,2-Dimethylbenzene ( <i>o</i> -xylene)	29.59	106	95-47-6	5.74

(Continued)

TABLE 17.5.1. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
22	Styrene	29.96	104	100-42-5	0.81
23	(1-Methylethyl)benzene	30.49	120	98-82-8	0.28
24	propylbenzene	31.81	120	103-65-1	3.09
25	1-Ethyl-3-methylbenzene	32.07	120	620-14-4	1.03
26	1-Ethyl-4-methylbenzene	32.19	120	622-96-8	0.55
27	$\delta$ -4-Carene?	32.84	136	554-61-0	0.36
28	1-Ethyl-2-methylbenzene	33.01	120	611-14-3	2.06
29	1,3,5-Trimethylbenzene	33.57	120	108-67-8	1.04
30	1-Propenylbenzene	34.00	118	637-50-3	3.19
31	1-Ethenyl-3-methylbenzene	34.08	118	100-80-1	0.33
32	5-Methyl-3-(1-methylethenyl)cyclohexene	34.39	136	56816-08-1	0.43
33	1,2,3-Trimethylbenzene	34.90	120	526-73-8	1.87
34	1-Methyl-3-(1-methylethyl)benzene	35.16	134	535-77-3	0.55
35	1-Methyl-3-propylbenzene	35.35	134	1074-43-7	1.85
36	1,4-Diethylbenzene	35.55	134	105-05-5	0.63
37	1-Methyl-4-(2-propenyl)benzene	35.79	132	3333-13-9	0.72
38	1-Methyl-4-propylbenzene	36.16	134	1074-55-1	5.39
39	1,3,8- <i>p</i> -Menthatriene	36.39	134	21195-59-5	0.36
40	Indene	36.61	116	95-13-6	2.92
41	1-Methyl-2-(2-propenyl)benzene	36.99	132	1587-04-8	0.88
42	4-Ethyl-1,2-dimethylbenzene	37.68	134	934-80-5	2.52
43	2-Ethenyl-1,4-dimethylbenzene	38.39	132	2039-89-6	1.48
44	4-Ethenyl-1,2-dimethylbenzene	38.52	132	27831-13-6	1.72
45	Phenol	38.66	94	108-95-2	1.61
46	2,4-Dimethylstyrene	38.85	132	2234-20-0	0.76
47	1-Methyl-4-(1-methylpropyl)benzene	39.06	148	1595-16-0	0.23
48	2,3-Dihydro-4-methyl-1H-indene	39.54	132	824-22-6	0.36
49	1,4-Dihydronaphthalene	40.01	130	612-17-9	1.34
50	2-Methylphenol	40.24	108	95-48-7	0.46
51	2-Methylindene	40.48	130	2177-47-1	2.50
52	Azulene?	41.19	128	275-51-4	0.28
53	1,2-Dihydro-3-methylnaphthalene	41.54	144	2717-44-4	0.20
54	1,2,3,4-Tetrahydro-2-methylnaphthalene	41.72	146	3877-19-8	0.12
55	Naphthalene	42.16	128	91-20-3	1.20
56	1-Ethenyl-2,3-dihydro-1H-indene	43.02	144	51783-46-1	0.28
57	1,2-Dihydro-4-methylnaphthalene	43.51	144	4373-13-1	0.41
58	2,3-Dimethyl-1H-indene	43.85	144	4773-82-4	1.25
59	1,2-Dihydro-6-methylnaphthalene	44.60	144	2717-47-7	0.50
60	2-Methylnaphthalene	45.39	142	91-57-6	0.91
61	1-Methylnaphthalene	45.93	142	90-12-0	0.85
62	2-Ethenylnaphthalene	47.50	154	827-54-3	0.31

TABLE 17.5.1. *cont'd*

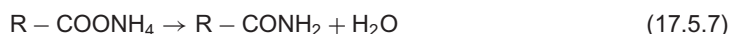
No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent pyrolysate
63	2-Ethyl-naphthalene	48.06	156	939-27-5	0.37
64	1,7-Dimethylnaphthalene	48.34	156	575-37-1	0.24
65	2,6-Dimethylnaphthalene	48.75	156	581-42-0	0.41
66	1,5-Dimethylnaphthalene	48.89	156	571-61-9	0.27
67	1,3-Dimethylnaphthalene	49.92	156	575-41-7	0.13
68	3-Methyl-1,1'-biphenyl	50.14	168	643-93-6	0.21
69	2,3-Dihydro-3,3-dimethyl-1H-indene	50.31	160	26465-81-6	0.77
70	7-Methylindan-1-one	50.41	146	39627-61-7	0.31
71	1,4,5-Trimethylnaphthalene	51.25	170	2131-41-1	0.15
72	Fluorene	53.71	166	86-73-7	0.28
73	2,3-Dihydro-3,4,7-trimethyl-1H-inden-1-one	54.44	174	35322-84-0	0.34
74	2,3-Dihydro-4,7-dimethyl-1H-inden-1-one	54.65	160	5037-60-5	0.92
75	1,1-Diphenylethylene	56.17	180	530-48-3	0.09
76	1,2,3,4-Tetrahydro-5,7-dimethylnaphthalene	56.40	160	21693-54-9	0.26
77	2-Methyl-9H-fluorene	56.55	180	1430-97-3	0.07
78	9-Methyl-9H-fluorene	56.67	180	2523-37-7	0.10
79	Phenanthrene	59.05	178	85-01-8	0.09
80	Anthracene	59.29	178	120-12-7	0.08

$T_{eq} = 900\text{ }^{\circ}\text{C}$ ,  $\beta = 10\text{ }^{\circ}\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280\text{ }^{\circ}\text{C}$ . The pyrolysate was analyzed under conditions given in Table 4.6.1. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 17.5.1. Peak identification was done based on their mass spectrum and the evaluation of the mole percent was obtained based on peak areas.

As shown in Table 17.5.1, most compounds seen in the pyrogram of hexa-2,4-dienoic acid potassium salt are aromatic compounds. Several fragments consisting mainly of small alkenes and alkadienes were also generated. The formation of many aromatic compounds was favored by the presence of the two double bonds in the acid molecule. Although not analyzed, it is likely that even heavier PAHs were present in the pyrolysate.

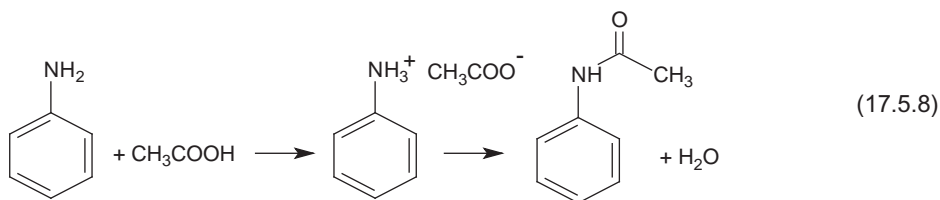
### Pyrolysis of ammonium salts

A special behavior in thermal decomposition is seen for the ammonium salts of carboxylic acids. The typical reaction of ammonium salts at temperatures around  $150\text{ }^{\circ}\text{C}$  is the formation of amides. The reaction can be written as follows:

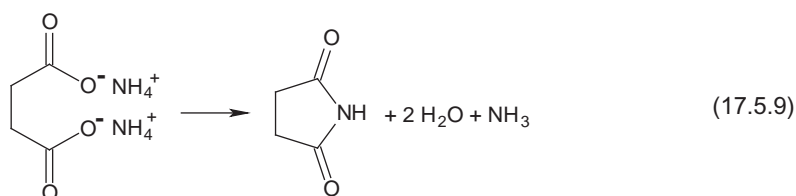


However, the decomposition is sometimes associated with other reactions [63]. Ammonium acetate does generate at about  $250\text{ }^{\circ}\text{C}$  high yields of acetamide, while ammonium formate generates HCN, CO,  $\text{NH}_3$ , etc. By pyrolysis at higher temperatures, the amides start decomposing, generating various products depending on the nature of the acid (see Section 19.6). The ammonium salts of dibasic acids typically form imides (e.g., succinimide from succinic acid).

The reaction of ammonium salts can also be extended to some amine salts. For example, acetic acid and aniline (which are assumed to form a salt) generate by heating acetanilide:



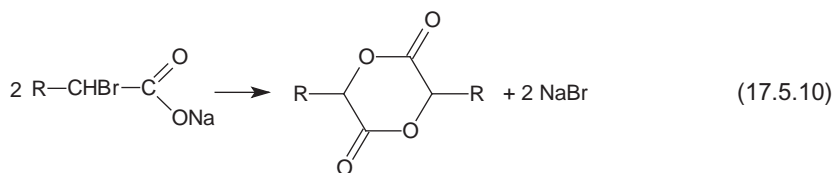
When the formation of stable imides is possible, both monoammonium salts and diammonium salts of dibasic acids have the tendency, when heated, to eliminate water and ammonia with the formation of these stable compounds. As an example, ammonium succinate is transformed into succinimide by heating around 200 °C in a reaction as shown below:



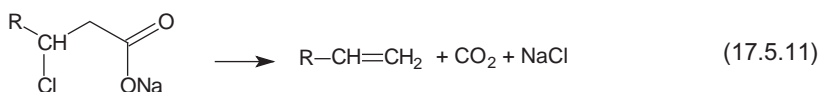
The reaction is characteristic for other ammonium salts of dicarboxylic acids capable of forming stable cycles of five or six atoms, such as ammonium isopropylsuccinate, ammonium glutarate, ammonium citraconate [13]. Ammonium oxalate generates a complex pyrolysate containing oxamide,  $\text{NH}_3$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{N}_2$ ,  $\text{HCN}$ , char.

### Pyrolysis of salts from acids with additional functional groups

A special place in acid salts thermal decompositions is played by the salts of acids that also contain a halogen atom in the molecule. Due to the large enthalpy of formation of many inorganic salts (e.g.,  $\text{NaCl}$  in solid phase has  $\Delta H = -98.26 \text{ kcal/mol}$ ) and due to their high stability at elevated temperatures, many pyrolysis processes tend to take place with the salt elimination, as shown below for the pyrolysis of a salt of an  $\alpha$ -bromo acid that leads to the formation of a substituted 1,4-dioxane-2,5-dione (lactide) [13]:



The salts of  $\beta$ -halogenated acids have the tendency to eliminate  $\text{CO}_2$  and the inorganic salt of the halogen and to form an alkene, as shown in the reaction below for a chlorinated compound:



## 17.6. THIO ACIDS

### General aspects

The replacement of the oxygen atom with sulfur in the formula of an organic acid generates thio acids. Thioic acids have the oxygen atom from the OH group of the carboxyl replaced and have the formula  $RC(=O)SH$  (e.g., thioacetic acid, or acetyl mercaptan  $CH_3-C(=O)SH$ ), and dithionic acids have both oxygen atoms replaced and have the formula  $RC(=S)SH$ .

Thioacetic acid by thermal decomposition generates mainly sulfur and acetaldehyde. Thermal decomposition of most dithionic acids typically generates  $H_2S$ , sulfur, and hydrocarbons. Thermal decomposition of Na salt of thiobenzoic acid generates tetraphenylthiophene [64].

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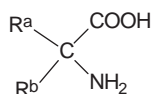
## CHAPTER 18

*Pyrolysis of Amino Acids and Small Peptides***18.1. AMINO ACIDS****General aspects**

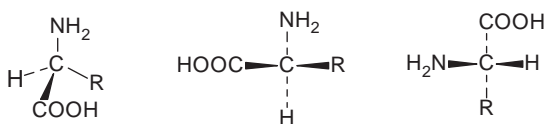
Amino acids are organic compounds that contain in their molecule the functional groups  $\text{NH}_2$  and  $\text{COOH}$ . The two groups can be attached to the same carbon atom (in  $\alpha$ -amino acids), to vicinal carbons (in  $\beta$ -amino acids), etc. Certain  $\alpha$ -amino acids represent the building blocks of peptides and proteins, which are polymeric materials formed by water elimination between  $\alpha$ -amino acid molecules. Besides the amino acids that are protein constituents, many other amino acids occur naturally in living systems. Synthetic amino acids are also common compounds. The subject of amino acids pyrolysis is of special environmental interest, being related to the processes taking place during the incineration of various biological samples and of municipal waste. Also, the exposure of food to elevated temperatures may lead to the pyrolysis of its amino acids constituents, a process related to important health issues.

 **$\alpha$ -Amino acids**

The general formula of  $\alpha$ -amino acids allows two different substituents  $\text{R}^a$  and  $\text{R}^b$  to be connected to the carbon atom bearing the functional groups  $\text{NH}_2$  and  $\text{COOH}$  (the  $\alpha$ -carbon). Although, acids with the two  $\text{R}^a$  and  $\text{R}^b$  radicals containing one or more carbon atoms are known, they are less common. Most common  $\alpha$ -amino acids, and in particular those present in proteins, have hydrogen as one of the R substituents. The names and the structures of the  $\alpha$ -amino acids typically present in proteins are shown in Table 18.1.1.



Except for glycine all the other  $\alpha$ -amino acids with one hydrogen attached to the  $\alpha$ -carbon have chiral molecules. The L (S) configuration for an  $\alpha$ -amino acid is shown below:

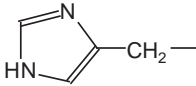
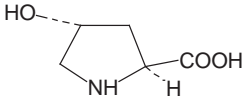
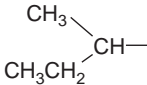
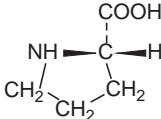
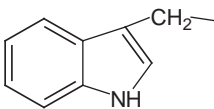
L- $\alpha$ -amino acids (S)

Most  $\alpha$ -amino acids present in proteins have the L configuration.

$\alpha$ -Amino acid thermal stability is different from acid to acid. Some acids such as glutamic acid are completely pyrolyzed at  $400^\circ\text{C}$ . Levels of 1% undecomposed amino acids were detected at  $500^\circ\text{C}$  for proline, at  $600^\circ\text{C}$  for glycine, and at  $700^\circ\text{C}$  for valine and leucine. Alanine was found undecomposed at 0.4% level even at  $800^\circ\text{C}$  [1]. The decomposition reactions follow several pathways [2–8]. In some reactions, the whole molecule is fragmented, eliminating  $\text{CO}_2$  and  $\text{NH}_3$  and forming, if possible, alkenes

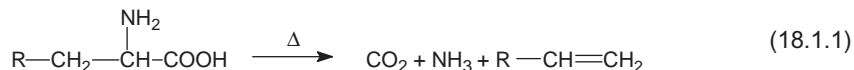


TABLE 18.1.1. *Amino acids present in proteins*

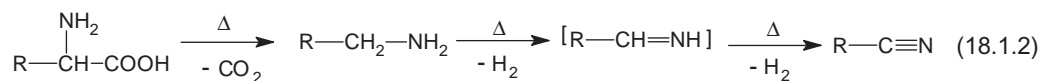
Name	Abbreviation (three-letter)	Abbreviation (one-letter)	Radical R connected to the $\alpha$ -carbon*	MW	Formula
Alanine	Ala	A	$\text{CH}_3-$	89.09	$\text{C}_3\text{H}_7\text{NO}_2$
Arginine	Arg	R	$\text{HN}=\text{C}(\text{H}_2\text{N})\text{NHCH}_2\text{CH}_2\text{CH}_2-$	174.20	$\text{C}_6\text{H}_{14}\text{N}_4\text{O}_2$
Asparagine	Asn	N	$\text{H}_2\text{N}-\text{CO}-\text{CH}_2-$	132.12	$\text{C}_4\text{H}_8\text{N}_2\text{O}_3$
Aspartic acid	Asp	D	$\text{HOOC}-\text{CH}_2-$	133.10	$\text{C}_4\text{H}_7\text{NO}_4$
Cysteine	Cys	C	$\text{HS}-\text{CH}_2-$	121.16	$\text{C}_3\text{H}_7\text{NO}_2\text{S}$
Cystine	Cys-Cys		$-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-$	240.30	$\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4\text{S}_2$
Glutamic acid	Glu	E	$\text{HOOC}-\text{CH}_2\text{CH}_2-$	147.13	$\text{C}_5\text{H}_9\text{NO}_4$
Glutamine	Gln	Q	$\text{H}_2\text{N}-\text{CO}-\text{CH}_2\text{CH}_2-$	146.15	$\text{C}_5\text{H}_{10}\text{N}_2\text{O}_3$
Glycine	Gly	G	$\text{H}-$	75.07	$\text{C}_2\text{H}_5\text{NO}_2$
Histidine	His	H		155.16	$\text{C}_6\text{H}_9\text{N}_3\text{O}_2$
Hydroxylysine	Hyl		$\text{H}_2\text{N}-\text{CH}_2-\text{CH}(\text{OH})-(\text{CH}_2)_2-$	162.19	$\text{C}_6\text{H}_{14}\text{N}_2\text{O}_3$
			Hydroxyproline*	Hyp	
				131.13	$\text{C}_5\text{H}_9\text{NO}_3$
Isoleucine	Ile	I		131.17	$\text{C}_6\text{H}_{13}\text{NO}_2$
Leucine	Leu	L	$(\text{CH}_3)_2\text{CHCH}_2-$	131.17	$\text{C}_6\text{H}_{13}\text{NO}_2$
Lysine	Lys	K	$\text{H}_2\text{N}-(\text{CH}_2)_4-$	146.19	$\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$
Methionine	Met	M	$\text{CH}_3\text{SCH}_2\text{CH}_2-$	149.21	$\text{C}_5\text{H}_{11}\text{NO}_2\text{S}$
Phenylalanine	Phe	F	$(\text{C}_6\text{H}_5)-\text{CH}_2-$	165.19	$\text{C}_9\text{H}_{11}\text{NO}_2$
Proline*	Pro	P		115.13	$\text{C}_5\text{H}_9\text{NO}_2$
Serine	Ser	S	$\text{HO}-\text{CH}_2-$	105.09	$\text{C}_3\text{H}_7\text{NO}_3$
Threonine	Thr	T	$\text{CH}_3-\text{CH}(\text{OH})-$	119.12	$\text{C}_4\text{H}_9\text{NO}_3$
Tryptophan	Trp	W		204.22	$\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2$
Tyrosine	Tyr	Y	$\text{HO}-(\text{C}_6\text{H}_4)-\text{CH}_2-$	181.19	$\text{C}_9\text{H}_{11}\text{NO}_3$
Valine	Val	V	$(\text{CH}_3)_2\text{CH}-$	117.15	$\text{C}_5\text{H}_{11}\text{NO}_2$

\*Whole formulas are shown for proline and hydroxyproline.

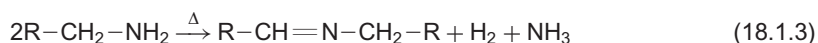
or other fragment hydrocarbons, as shown in the following reaction:



One other path is the decarboxylation reaction, followed by reactions typical for amines. In the reaction below, the amine eliminates hydrogen and forms a nitrile:

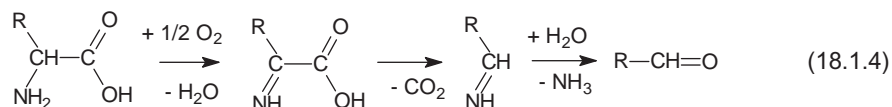


Following the decarboxylation, the amines also can undergo a different decomposition path, as shown in the reaction below:



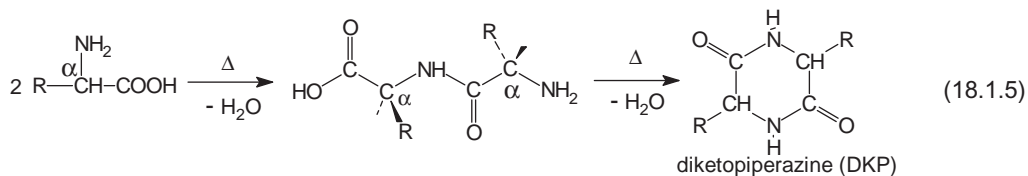
The compounds of the type  $\text{R}-\text{CH}=\text{N}-\text{CH}_2-\text{R}$  and also  $\text{R}'=\text{C}=\text{N}-\text{CH}_2-\text{R}$  are formed mainly from aliphatic amino acids (Ala, Val, Leu, Ile).

Particularly when oxygen is present during pyrolysis, amino acids also can undergo a Strecker type degradation as shown below:

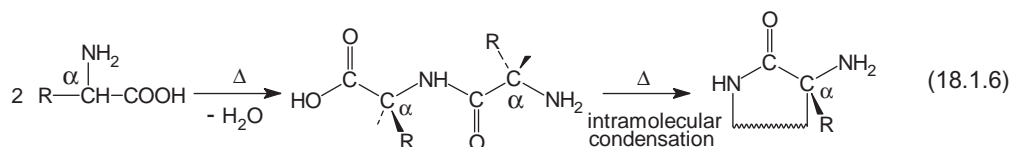


This reaction explains the presence of aldehydes in some amino acids pyrolysates. The role of the oxidant can be played by other molecules besides oxygen.

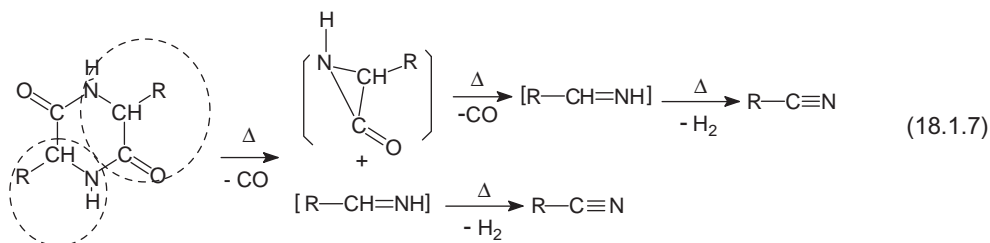
A typical reaction during pyrolysis is water elimination between two amino acid molecules leading to a dipeptide. Depending on the pyrolysis conditions, the dipeptide can be detected in the pyrolysate. The formation of a peptide as an intermediate step in amino acid pyrolysis has been evaluated in a number of studies [9]. It was suggested that further amino acid pyrolysis proceeds with an intramolecular condensation of dipeptides. However, the formation of diketopiperazines (DKP) from peptides takes place with a higher yield than their formation from single amino acids (see Section 18.3). The intramolecular condensation can take place by different reactions, a common path leading to the formation of DKP as shown below:



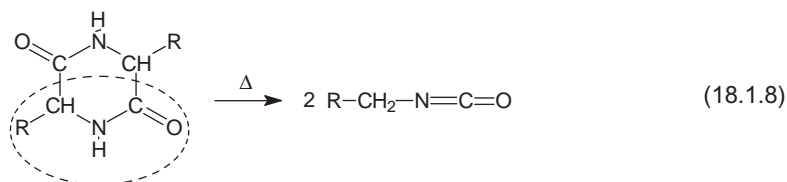
Other intramolecular condensation routes are possible for the intermediate dipeptides, and the formation of cycles is common. One path is suggested in the following reaction:



DKP may undergo further pyrolysis decomposing by different mechanisms. One possible decomposition route is shown below:



Another potential decomposition route leads to the formation of isocyanates, as shown in the following reaction:



The condensation reaction with the formation of a dipeptide can continue with the formation of a tripeptide or even a more complex molecule. These condensation reactions are followed by further decompositions including water elimination and intramolecular condensations. This type of process explains the presence in the pyrolysates of heavier molecules compared to the initial amino acid. The tendency of formation of compounds with high thermal stability during pyrolysis may explain the formation of some polycyclic aromatic molecules from certain amino acids.

The pyrolysis results for some specific  $\alpha$ -amino acids are further discussed in this section. The information was obtained for a number of amino acids which were pyrolyzed in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ . The analysis of pyrolysate was done exclusively by GC/MS under conditions given in Table 4.6.1. The following figures show the resulting pyrograms for individual amino acids, and the associated tables give the compound identifications and their relative molar content in 100 moles of pyrolysate. The mole percent of the main pyrolysis products in these tables are indicated in bold numbers. The calculation of the mole percent for each amino acid was obtained based solely on peak areas. During amino acids pyrolysis, some small molecules such as  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{HCN}$ , and  $\text{NH}_3$  are common pyrolysis products. These compounds were not captured in the mole percent composition since they were not detected during pyrolysate analysis due to the mass spectrometer settings, which allows only masses higher than 28 a.u. (and lower than 550 a.u.) to be detected. Also, a certain amount of char was always generated by amino acids pyrolysis. This char was not analyzed and was not included in the calculation of the mole percent of individual components of the pyrolysate.

The simplest  $\alpha$ -amino acid is glycine (Gly), which melts around  $240^\circ\text{C}$  with decomposition. Heated around  $205^\circ\text{C}$  in melted naphthalene for about 3 h, glycine loses one water molecule and gives glycylglycine, which can be hydrolyzed back to glycine. At  $260^\circ\text{C}$  the decomposition occurs with the formation of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$ . At  $400^\circ\text{C}$  formation of  $\text{HCHO}$  is the main process, and  $\text{CO}$  and  $\text{HCN}$  also evolve [10]. Pyrolyzed at  $900^\circ\text{C}$ , 1.0 mg glycine generates the pyrogram shown in Figure 18.1.1. The identification of the compounds in the pyrogram is given in Table 18.1.2 as a function of peak retention times.

Many products in glycine pyrolysate are explained by reactions 18.1.1–18.1.8. Formaldehyde, which is detected at  $400^\circ\text{C}$  pyrolysis, was not detected as pyrolysis product at  $900^\circ\text{C}$ . Among the more complex molecules, the largest pyrolysate constituents are hydantoin or 2,4-imidazolidinedione, DKP or 2,5-piperazindione, and 3-methyl-2,5-piperazindione or 3-methyl-diketopiperazine. The formation of 3-methyl-2,5-piperazindione and of the triazine indicates that pyrolysis of glycine is a process

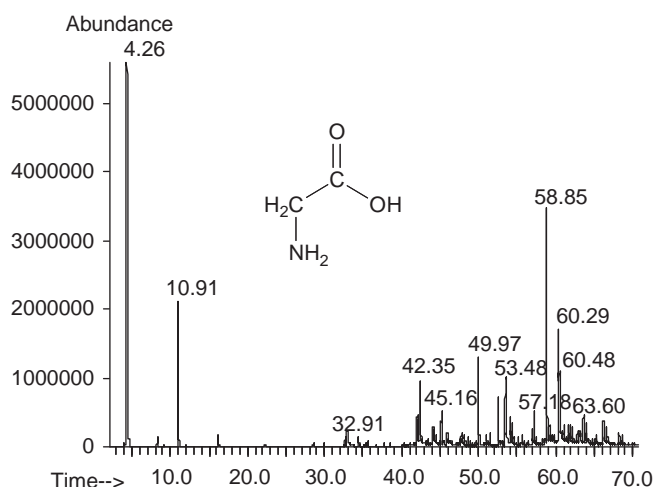
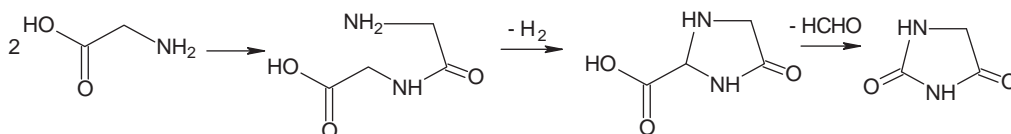


FIGURE 18.1.1. Pyrogram obtained at 900°C for glycine (MW = 75).

more complex than described by reactions 18.1.1–18.1.8. For example, the formation of 2,4-imidazolidinedione (hydantoin) can be explained by a reaction as shown below:



Other studies on glycine pyrolysis have been reported in the literature [2,11–14].

Several  $\alpha$ -amino acids typically found in proteins have simple aliphatic hydrocarbon radicals R connected to the  $\alpha$ -carbon. These amino acids include alanine (Ala), valine (Val), isoleucine (Ile), and leucine (Leu). These compounds are chemical homologs differing one from each other (and from glycine) by a  $\text{CH}_2$  group. L-Isoleucine and L-leucine are isomers. An investigation on thermal behavior of alanine, valine, isoleucine, leucine (and also of proline) was performed by thermogravimetry in the range of temperatures 30–400 °C, and kinetic equations for the decomposition in solid phase were established [15]. Alanine and  $\beta$ -alanine pyrolysis also is reported in the literature [16].

The pyrograms of the four amino acids Ala, Val, Ile, and Leu at 900 °C are shown in Figure 18.1.2 (L-alanine), Figure 18.1.3 (L-valine), Figure 18.1.4 (L-isoleucine), and Figure 18.1.5 (L-leucine).

The peak identification for alanine pyrolysis is given in Table 18.1.3. The main pyrolysis products are explained by reactions 18.1.1–18.1.8. Some compounds in alanine pyrolysate are homologous to those formed in glycine pyrolysis. Examples include the following pairs: methyl isocyanate (for Gly) and ethyl isocyanate (for Ala), DKP (for Gly) and 3,6-dimethyl-2,5-diketopiperazine (for Ala). However, even in the case of homologous compounds, the peak intensities (indicative of the mole percent of each compound in the pyrogram) are not very similar. Overall, glycine has a more complex pyrogram than alanine, with several nitriles and a number of heterocycles for which the expected homologs in alanine pyrolysate are absent.

The peak identification for valine pyrolysate (as obtained with mass spectral library searches) is given in Table 18.1.4, and the peak identification for isoleucine and leucine pyrolysates is given for both amino acids in Table 18.1.5.

Pyrolysis of valine on one hand and isoleucine and leucine on the other generates a number of compounds with homologous structures. Isoleucine and leucine generate isomers of the same compound. Some of these compounds are shown in Table 18.1.6.

Other compounds in the pyrolysates of valine, isoleucine, and leucine do not have homologous or isomeric equivalents. For example, the formation of 3,6-diisopropyl-2,5-dioxomorpholine in the valine

TABLE 18.1.2. Peak identification as a function of retention time for the pyrogram of glycine in Figure 18.1.1 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.27	44	124-38-9	<b>54.71</b>
2	Methyl isocyanate	8.26	57	624-83-9	1.71
3	Acetonitrile	10.91	41	75-05-8	<b>10.76</b>
4	Propanenitrile	16.26	55	107-12-0	1.71
5	Acetamide	32.91	59	60-35-5	1.59
6	Mixture of three compounds	42.02	111	N/A	0.99
7	1-Methyl-2,5-pyrrolidinedione	42.19	113	121-07-9	0.48
8	1,4-Cyclohexandione	42.36	112	637-88-7	1.94
9	2-Ethyl-2-methyl-1,3-cyclopentanedione?	44.08	140	25112-87-2	0.21
10	3,4-Dimethyl-1H-pyrrole-2,5-dione	44.22	125	17825-86-4	0.21
11	2-(dimethylamino)pyrrolyn-5-one	44.31	126	68321-93-7	0.18
12	3-Methyl-2,5-pyrrolidin-2,5-dione	45.11	113	5615-90-0	0.26
13	2,5-Pyrrolidindione (succinimide)	45.16	99	123-56-8	1.07
14	2,4(1H,3H)-pyrimidinedione	45.91	112	66-22-8	0.20
15	2,3,6-Trimethyl-4(3H)-pyrimidinone	47.74	138	32363-51-2	0.16
16	5,6-Dihydro-3-methyluracil	48.96	128	N/A	0.17
17	3-Methyl-2,4-imidazolidinedione (3-methylhydantoin)	49.97	114	6843-45-4	2.06
18	5-Methyl-2,4-imidazolidinedione (5-methylhydantoin)	52.54	114	616-03-5	1.30
19	2,4-Imidazolidinedione (hydantoin)	53.48	100	461-72-3	<b>3.49</b>
20	N-Methylacetamide	54.16	73	79-16-3	1.08
21	5-Ethyl-2,4-imidazolidinedione	54.38	128	15414-82-1	0.37
22	Mixture	56.93	153	N/A	0.21
23	1-Methyldihydro-2,4(1H,3H)-pyrimidinedione	57.18	128	696-11-7	0.65
24	3-Methyl-2,5-piperazindione	58.85	128	N/A	<b>5.25</b>
25	Unknown	59.16	152	N/A	0.25
26	2,5-Piperazinedione	60.29 60.48	114	106-57-0	<b>6.62</b>
27	N-Methyl-3,5-dihydroxyaniline	61.73	139	40248-01-9	0.26
28	1-Ethyl-2,5-pyrrolidinedione	61.88	127	2314-78-5	0.30
29	6-Methyl-1,2,4-triazine-3,5(2H,4H)-dione	62.68	127	932-53-6	0.28
30	Unknown	63.60	193	N/A	0.31
31	Unknown	64.05	149	N/A	0.22
32	2,4,6-Trimethyl-7-oxo-4,7-dihydro-1,2,4-triazolo-[3,2-c]-1,2,4-triazine	66.20	179	25623-78-3	0.46
33	Unknown	66.66	193	N/A	0.22
34	Unknown	68.24	193	N/A	0.17
35	Unknown	68.57	207	N/A	0.16

Note: Bold numbers in this and subsequent tables indicate main pyrolysis products.

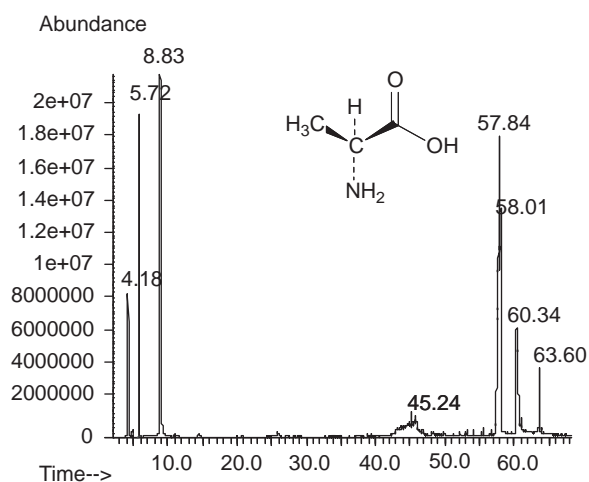


FIGURE 18.1.2. Pyrogram obtained at 900°C for L-alanine (MW = 89).

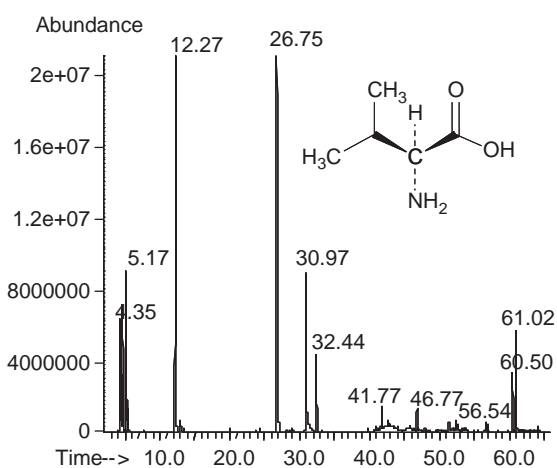


FIGURE 18.1.3. Pyrogram obtained at 900°C for L-valine (MW = 117).

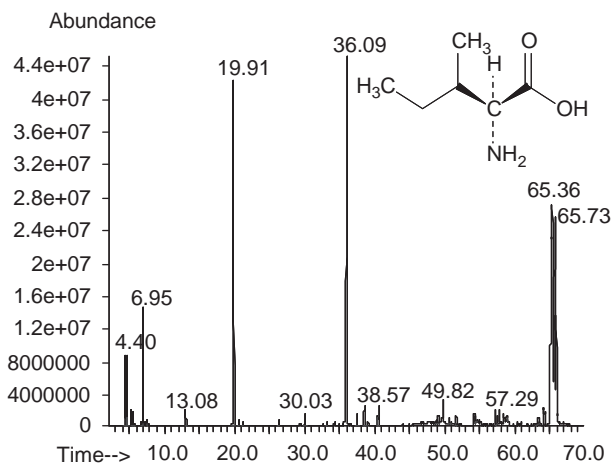


FIGURE 18.1.4. Pyrogram obtained at 900°C for L-isoleucine (MW = 131).

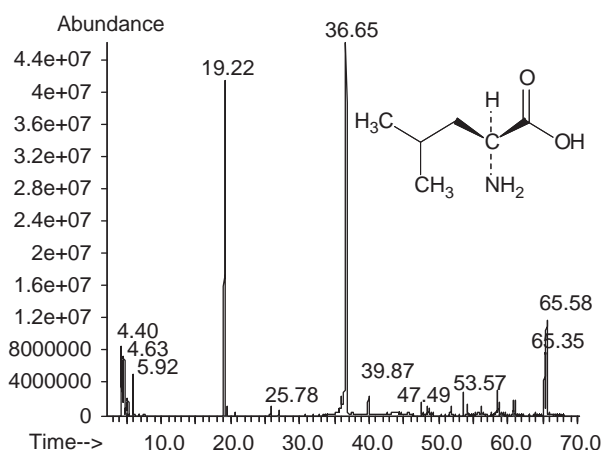


FIGURE 18.1.5. Pyrogram obtained at 900°C for L-leucine (MW = 131).

TABLE 18.1.3. Peak identification as a function of retention time for the pyrogram of alanine in Figure 18.1.2 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.19	44	124-38-9	<b>13.85</b>
2	Acetaldehyde	5.72	44	75-07-0	<b>16.01</b>
3	Ethyl isocyanate	8.84	71	109-90-0	<b>22.50</b>
4	Butenal	19.99	70	123-73-9	0.15
5	1-(1-butenyl)aziridine?	25.82	97	80839-92-5	0.31
6	2-Methylpyridine	29.15	93	109-06-8	0.11
7	Unknown	38.81	125	N/A	0.05
8	2-Ethyl-5-methylpyridine	38.81	121	18113-81-0	0.06
9	1,2-Propandiamine	44.61	74	78-90-0	<b>2.71</b>
10	4,4-Dimethyl-2,5-dioxo-1-vinylimidazolidine?	44.83	154	31787-67-4	0.85
11	3-Ethyl[1.2.4]triazolo[4.3-a]pyridine?	45.24	147	4919-17-9	0.92
12	Alanine	45.84	89	56-41-7	1.62
13	Cycloglycylalanine	53.18	142	N/A	0.11
14	N-Ethyl-propanamide	54.05	101	5129-72-6	0.23
15	1,3-Dimethyl-2,4,5-trioxoimidazolidine	56.63	170	10319-61-6	0.11
16	3,6-Dimethylpiperazine-2,5-dione	57.84	142	5625-46-7	<b>30.76</b>
		58.01			
17	Unknown	60.33	152	N/A	3.93
18	2-Amino-5,8-dihydro-4,6,7(1H)-pteridintrione	60.33	195	492-1-5	4.28
19	Unknown	63.60	193	N/A	1.39
20	Unknown	63.90	207	N/A	0.04

pyrolysate did not have an equivalent in the pyrolysates of isoleucine and leucine. A number of components that are present at low levels in pyrolysates of valine, isoleucine, and leucine were not identified.

One finding regarding the pyrograms of alanine, valine, isoleucine, and leucine is that in each pyrogram generated under conditions described in Table 4.6.1, the corresponding DKP generated more

TABLE 18.1.4. Peak identification as a function of retention time for the pyrogram of valine in Figure 18.1.3 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.35	44	124-38-9	4.67
2	Propane	4.59	44	74-98-6	2.73
3	Propene	4.69	42	115-07-1	8.28
4	2-Methyl-1-propene	5.18	56	115-11-7	<b>5.04</b>
5	2-Butene	5.51	56	590-18-1	0.89
6	2-Methylpropanal	12.26	72	78-84-2	<b>53.31</b>
7	2-Methylpropenal	12.97	70	78-85-3	0.84
8	2-Methylpropanenitrile (isobutyronitrile)	20.05	69	78-82-0	<b>0.39</b>
9	2-Methyl-N-(2-methylpropylidene)-1-propanamine	26.75	127	6898-82-4	<b>13.90</b>
10	2-Ethyl-3-methylbutanal?	28.68	114	26254-92-2	0.09
11	3,4-Dimethyl-3-pyrrolin-2-one	29.01	111	4030-22-2	0.16
12	2,5-Dimethyl-1-aza-bicyclo[2.2.1]heptane	30.97	125	N/A	4.98
13	1-Ethyl-2-methylpiperidine?	32.44	127	766-52-9	1.76
14	3-Isopropylidene-2,5-diketopiperazine	41.77	156	N/A	0.33
15	2-Methoxy-3-(1-methylethyl)pyrazine	46.77	152	25773-40-4	0.47
16	3,6-Diisopropyl-2,5-dioxomorpholine	56.54	199	9/5/2503	0.14
17	3,6-Diisopropylpiperazin-2,5-dione	60.50	198	5625-44-5	<b>2.03</b>
		61.02			

TABLE 18.1.5. Peak identification as a function of retention time for the pyrograms of isoleucine and leucine shown in Figures 18.1.4 and 18.1.5 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent in isoleucine	Mole percent in leucine
1	Carbon dioxide	4.40	44	124-38-9	7.37	8.79
2	Propene	4.67	42	115-07-1	5.82	8.60
3	2-Methyl-1-propene	5.27	56	115-11-7	0.97	1.25
4	1,3-Butadiene	5.42	54	106-99-0	—	0.20
5	2-Butene	5.46	56	624-64-6	0.86	—
6	3-Methyl-1-butene	5.92	70	563-45-1	—	<b>1.82</b>
7	2-Methyl-1-butene	6.95	70	563-46-2	<b>5.25</b>	—
8	Methacrolein	13.08	70	78-85-3	1.00	—
9	3-Methylbutanal	19.22	86	590-86-3	—	<b>36.34</b>
10	2-Methylbutanal	19.91	86	96-17-3	<b>29.99</b>	0.50
11	2-Butenal	20.60	70	123-73-9	—	0.38
12	2-Methylbutylamine	21.18	87	20626-52-2	0.56	—
13	Unknown	25.78	98	N/A	—	0.67
14	2-Methyl-butanenitrile	26.31	83	18936-17-9	<b>0.32</b>	—

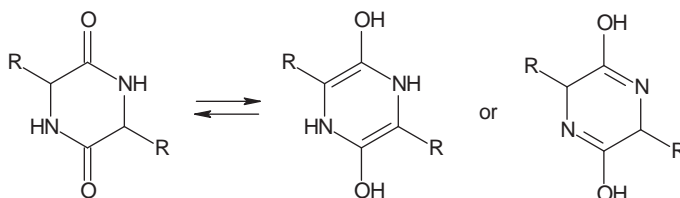
(Continued)



TABLE 18.1.5. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent in isoleucine	Mole percent in leucine
15	3-Methyl-butanenitrile	26.93	83	625-28-5	—	<b>0.40</b>
16	Unknown	30.03	113	N/A	0.53	—
17	4-Methyl-pentanenitrile	32.88	97	542-54-1	—	0.11
18	2-Methyl- <i>N</i> -(2-methylbutylidene)-1-butanamine	36.0	155	54518-97-7	<b>22.40</b>	—
19	3-Methyl- <i>N</i> -(3-methylbutylidene)-1-butanamine	36.65	155	35448-31-8	0.05	<b>34.21</b>
20	5-Aza-3,7-dimethylnona-1,4-diene	37.50	153	N/A	0.32	—
21	5-Aza-3,7-dimethylnona-1,5-diene	38.57	153	N/A	0.62	—
22	1,2,3,4-Tetrahydro-2,4-dioxo-5-pyrimidincarboxaldehyde	39.87	140	1195-08-0	—	0.50
23	Unknown	40.52	155	N/A	0.16	—
24	1,2,3,4-Tetrahydro-2,4-dioxo-5-pyrimidincarboxaldehyde (isomer)	40.60	140	N/A	0.61	—
26	<i>N</i> -Leucylglycine	54.18	188	615-82-7	—	0.66
27	<i>N</i> -Isoleucylglycine	54.26	188	N/A	0.23	—
26	Unknown	58.46	211	N/A	0.57	0.51
27	3,6-bis(2-methylpropyl)piperazine-2,5-dione	65.34 65.57	226	1436-27-7	—	<b>4.81</b>
28	3,6-bis(1-methylpropyl)piperazine-2,5-dione	65.36 65.72 65.93	226	N/A	<b>20.49</b>	—

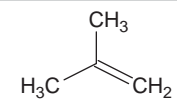
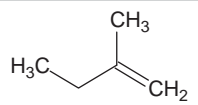
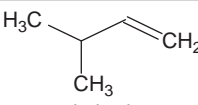
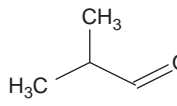
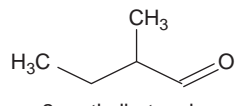
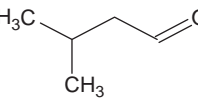
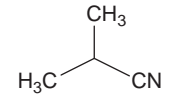
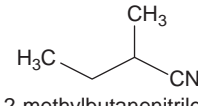
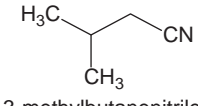
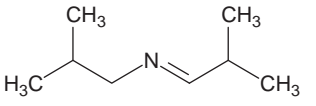
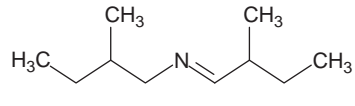
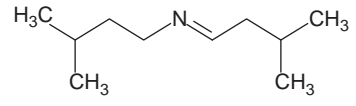
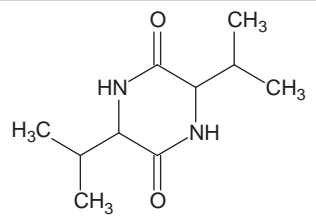
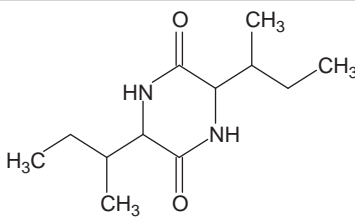
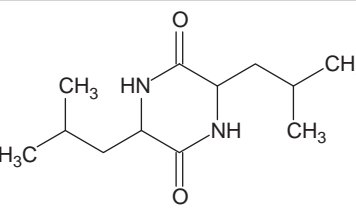
than one chromatographic peak (e.g., in the isoleucine pyrogram the peaks are at 65.36, 65.72, and 65.93 min). Typical for chromatographic separations, peaks with different retention times should not correspond to identical compounds. However these multiple peaks in the pyrogram show identical mass spectra. It is possible that the compound displays a keto-enol equilibrium as shown below:



Additional supporting data showing a single major constituent identified as a DKP were provided by the analysis of the silylated pyrolysates. DKP generate a single silylated derivative since only the enol form can be silylated. The mass spectra for 3,6-diisopropylpiperazin-2,5-dione 2 TMS resulting from valine and of 3,6-bis(1-methylpropyl)piperazine-2,5-dione 2 TMS resulting from isoleucine are shown in Figures 18.1.6 and 18.1.7, respectively. For a number of peaks between the two mass spectra, a difference of 28 a.u., indicating a difference of two CH<sub>2</sub> groups, can be seen.

The analysis of silylated pyrolysate of valine, isoleucine, and leucine did not show the presence of dipeptides Val-Val, Ile-Ile, or Leu-Leu, but showed the presence of some free amino acid.

TABLE 18.1.6. *Compounds with homologous structures in the pyrograms of valine, isoleucine, and leucine*

From valine	From isoleucine	From leucine
 2-methyl-1-propene	 2-methyl-1-butene	 3-methyl-1-butene
 2-methylpropanal	 2-methylbutanal	 3-methylbutanal
 2-methylpropanenitrile	 2-methylbutanenitrile	 3-methylbutanenitrile
 2-methyl-N-(2-methylpropylidene)-1-propanamine	 2-methyl-N-(2-methylbutylidene)-1-butanamine	 3-methyl-N-(3-methylbutylidene)-1-butanamine
 3,6-diisopropylpiperazine-2,5-dione	 3,6-bis(1-methylpropyl)-piperazine-2,5-dione	 3,6-bis(2-methylpropyl)-piperazine-2,5-dione

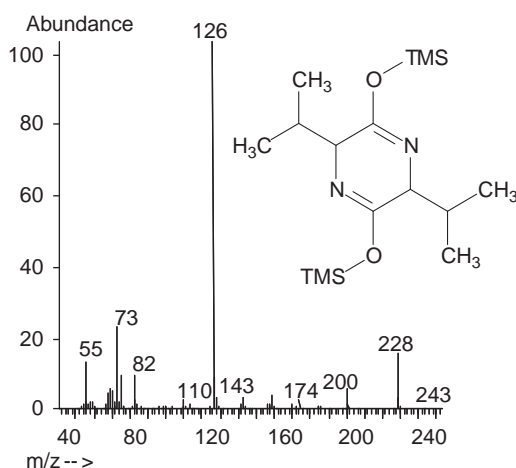


FIGURE 18.1.6. Mass spectrum of silylated 3,6-diisopropylpiperazin-2,5-dione (MW = 342).

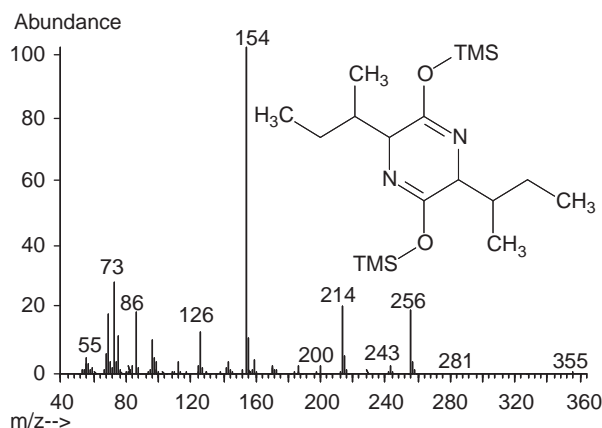


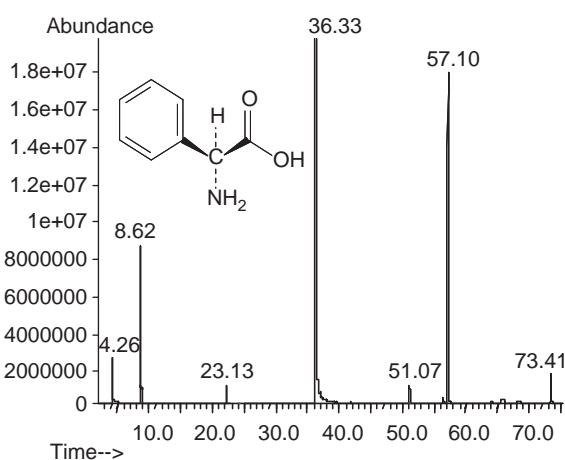
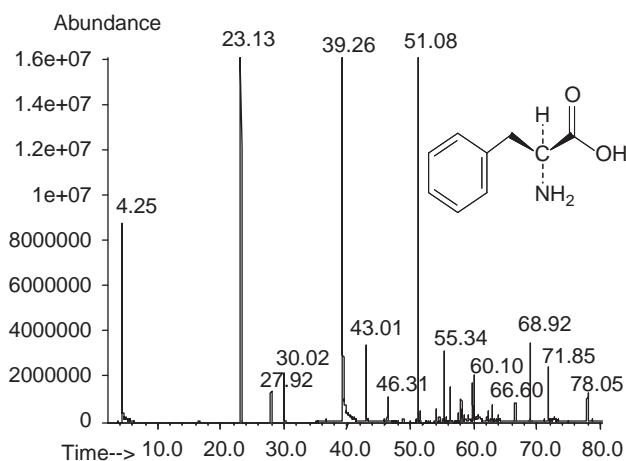
FIGURE 18.1.7. Mass spectrum of silylated 3,6-bis(1-methylpropyl)piperazine-2,5-dione (MW = 370).

Two other  $\alpha$ -amino acids that contain aromatic hydrocarbon type R substituents are phenylglycine (Pgl) and phenylalanine (Phe). Phenylglycine is not a typical protein constituent but is present, for example, as a side group in several cephalosporin antibiotics. The pyrogram generated at 900 °C for phenylglycine is shown in Figure 18.1.8, and that for phenylalanine is shown in Figure 18.1.9.

The peak identification for phenylglycine pyrolysate is given in Table 18.1.7, and the peak identification for phenylalanine pyrolysate is given in Table 18.1.8.

As shown in Tables 18.1.7 and 18.1.8, phenylglycine (Pgl) and phenylalanine (Phe) generate by pyrolysis a number of homologous compounds such as: benzylamine (for Pgl) and 2-phenylethylamine (for Phe), stilbene (for Pgl) and 1,3-diphenyl-1-butene (for Phe), dibenzylamine (for Pgl) and bis(2-phenylethyl)amine (for Phe).

The main decomposition path for the pyrolysis of phenylglycine and phenylalanine is a decarboxylation with the result of an amine formation. The reactions of the type 18.1.1–18.1.8 play a smaller role in phenylglycine and phenylalanine decomposition. The decarboxylation process is shown

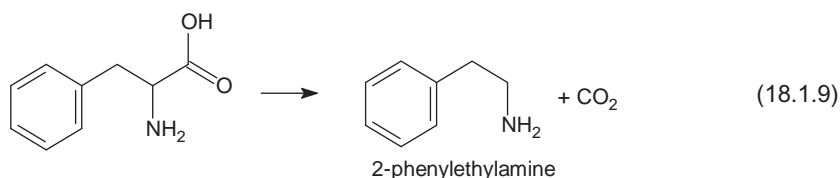
FIGURE 18.1.8. Pyrogram obtained at 900°C for *L*-phenylglycine (MW = 151).FIGURE 18.1.9. Pyrogram obtained at 900°C for *L*-phenylalanine (MW = 165).TABLE 18.1.7. Peak identification as a function of retention time for the pyrogram of phenylglycine shown in Figure 18.1.8 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.26	44	124-38-9	6.70
2	Unknown ( $CO_2$ ?)	8.62	44	N/A	7.29
3	Benzene	16.50	78	71-43-2	0.10
4	Toluene	23.13	92	108-88-3	0.85
5	Benzylamine	36.33	107	100-46-9	<b>76.77</b>
6	1,2-Diphenylethane (bibenzyl)	51.07	182	103-29-7	0.34
7	1,2-Diphenylethylene (stilbene)	56.35	180	588-59-0	0.13
8	Dibenzylamine	56.42	197	103-49-1	0.11
9	<i>N</i> -Benzylidenebenzylamine	57.10	195	780-25-6	<b>6.19</b>
10	2,4-Diphenyl-1-(2-phenylethyl)-1H-pyrrole?	65.81	323?	15811-39-9	0.40
11	2-Phenyl-1H-pyrrolo[2,3- <i>b</i> ]pyridine?	73.40	194	10586-52-4	1.11

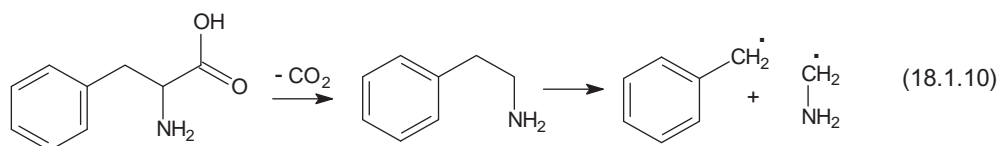
TABLE 18.1.8. Peak identification as a function of retention time for the pyrogram of phenylalanine shown in Figure 18.1.9 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.25	44	11469767	16.85
2	Toluene	23.13	92	10723521	<b>15.74</b>
3	Ethylbenzene	27.92	106	456957.7	0.67
4	Styrene	30.03	104	743794.2	1.09
5	2-Phenylethylamine	39.26	121	34873096	<b>51.23</b>
6	Benzyl nitrile (benzyl cyanide)	43.01	117	979014.4	1.44
7	3-Phenylpropanenitrile	46.31	131	288753.5	0.42
8	1,2-Diphenylethane (bibenzyl)	51.08	182	4243026	<b>6.23</b>
9	$\alpha$ -Methyl-bibenzyl	51.54	196	76233.71	0.11
10	1,3-Diphenylpropane	54.16	196	99757.06	0.15
11	Phenylpropanamide	55.34	149	856272.2	1.26
12	1,2,3,4-Tetrahydro-2-phenylnaphthalene	55.64	208	55027.85	0.08
13	$\alpha$ -Methyl-stilbene	56.35	194	255061.4	0.37
14	1,3-Diphenyl-1-butene	57.44	208	80238.01	0.12
15	3-(2-phenylethyl)benzonitrile	59.91	207	249452	0.37
16	bis(2-phenylethyl)amine	60.10	225	366645.2	0.54
17	1-Phenyl- <i>N</i> -(phenylmethylidene)-2-propanamine	62.19	223	78396.88	0.12
18	4-Styrylquinoline	62.90	231	124247	0.18
19	<i>N</i> -Methyl-benz[ <i>f</i> ]isoindole?	66.60	181	221676.6	0.33
20	11-Methyl-6-oxo-6H-isoindolo[2.1- <i>a</i> ]indol?	68.92	233	779780.5	1.15
21	2-Amino-5-phenylpyridine	70.46	170	33421-40-8	> 0.01
22	2,6-Diphenylpyridine	71.85	231	643351.8	0.95
23	Unknown	78.04	253	411548.8	0.60

below for phenylalanine:

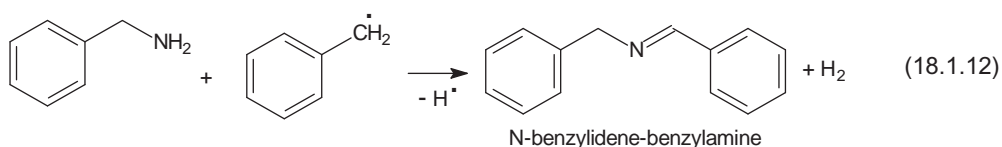
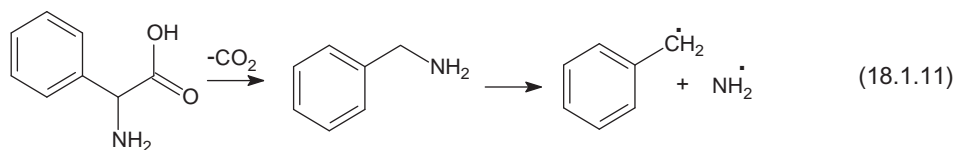


Other constituents present at high levels in the pyrolysate of phenylalanine are toluene and bibenzyl. The formation of these compounds can be explained by an initial reaction that generates benzyl radicals as shown below:



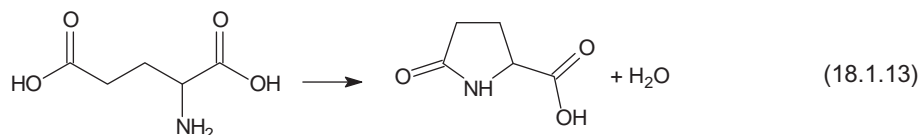
The benzyl radicals further react either with molecules of the acid or among themselves to form toluene, bibenzyl, as well as compounds such as  $\alpha$ -methyl-bibenzyl, 1,3-diphenylpropane,  $\alpha$ -methyl-stilbene, and 1,3-diphenyl-1-butene. Similar compounds or their lower homologs are present in phenylglycine pyrolysate but at lower levels.

In the pyrolysate of phenylglycine, another large constituent is *N*-benzylidene-benzylamine. The formation of this compound can be explained by reactions of the following type:



This type of reaction also occurs during phenylalanine pyrolysis to generate compounds such as 1-phenyl-*N*-(phenylmethylidene)-2-propanamine, but the resulting compounds are present at lower levels in the pyrolysate.

Another set of  $\alpha$ -amino acids contains one additional carboxyl group (not connected to the  $\alpha$ -carbon) in the molecule. This set is represented by two homologous acids, aspartic (Asp) and glutamic acid (Glu). The additional COOH group is connected to the  $\beta$  carbon for aspartic acid, and to the  $\gamma$  carbon for glutamic acid. At 300 °C glutamic acid generates mainly piperidine-2,6-dione, pyroglutamic acid, and pyrrolidin-2-one. The formation of pyroglutamic acid takes place by water elimination in a reaction shown as follows:



The pyrogram generated for L-aspartic acid at 900 °C is shown in Figure 18.1.10 and that for L-glutamic acid at 900 °C is shown in Figure 18.1.11.

The compound identifications are given in Table 18.1.9 for L-aspartic acid pyrolysate and in Table 18.1.10 for L-glutamic acid pyrolysate.

Although very similar in structure, aspartic and glutamic acid being homologs (one CH<sub>2</sub> difference), they do not generate any major homologous pyrolysis products. The main reaction of water elimination

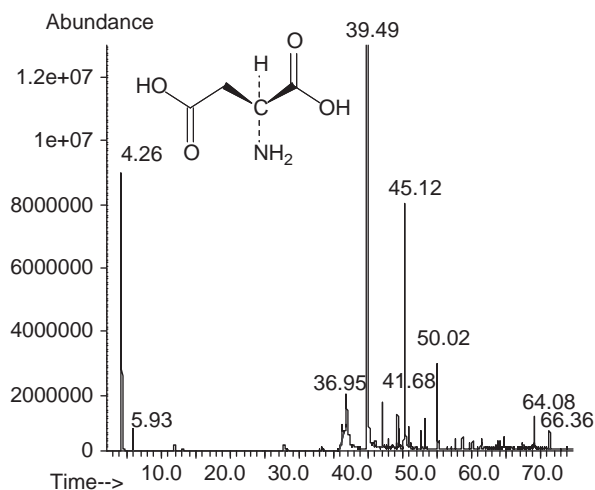


FIGURE 18.1.10. Pyrogram obtained at 900 °C for L-aspartic acid (MW = 133).

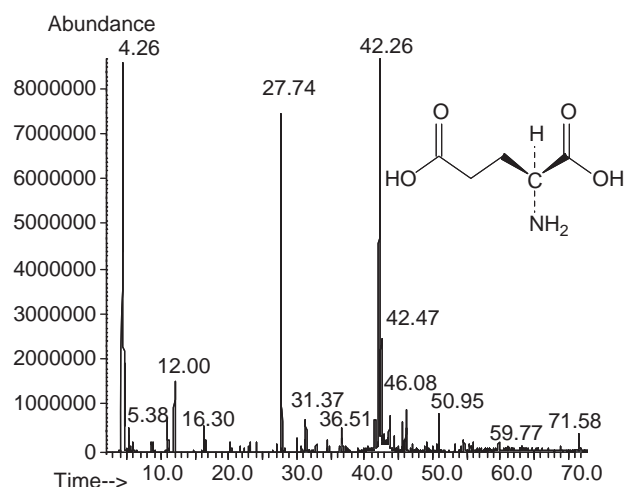
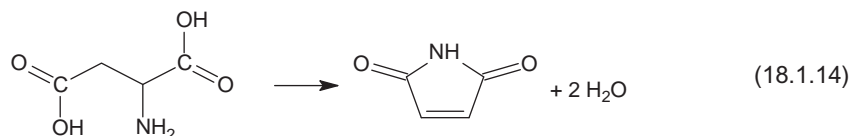


FIGURE 18.1.11. Pyrogram obtained at 900 °C for L-glutamic acid (MW = 147).

TABLE 18.1.9. Peak identification as a function of retention time for the pyrogram of aspartic acid shown in Figure 18.1.10 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ , not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.26	44	124-38-9	<b>32.48</b>
2	Acetaldehyde	5.93	44	75-07-0	1.11
3	Propenoic acid	27.90	72	79-10-7	0.64
4	2-Butenedioic acid	36.31	116	110-1-67	1.81
5	1-Ethyl-1H-pyrrole-2,5-dione	36.95	125	128-53-0	<b>5.53</b>
6	1H-Pyrrole-2,5-dione	39.49	97	541-59-3	<b>41.37</b>
7	6-Hydroxy-2(1H)-pyridinone?	41.68	111	626-06-2	0.78
8	2,5-Pyrolidinedione	45.12	99	123-56-8	<b>12.81</b>
9	2-Acetyl-1,4,5,6-tetrahydropyridine	50.02	125	25343-57-1	2.21
10	5-Methyl-2,4-imidazolidinedione	52.63	114	616-03-5	0.31
11	o-Cyanobenzoic acid	53.73	147	3839-22-3	0.21
12	2(1H)-pyridinone	59.25	95	142-08-5	0.22
13	A nitrile?	64.08	263	N/A	0.29
14	Unknown	66.36	224	N/A	0.23

for aspartic acid is not associated with  $CO_2$  elimination (although some  $CO_2$  is seen in the pyrogram) and takes place generating 1H-pyrrole-2,5-dione as follows:



An equivalent reaction for glutamic acid is associated with  $CO_2$  elimination (large peak in the pyrogram) leading to pyrrole:

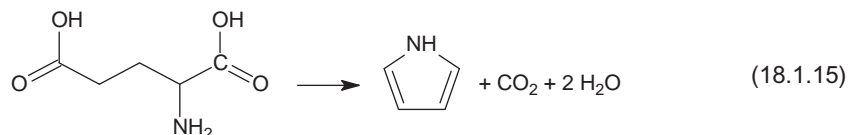
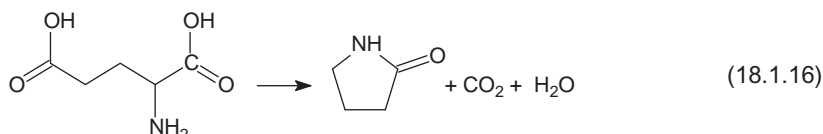


TABLE 18.1.10. Peak identification as a function of retention time for the pyrogram of glutamic acid shown in Figure 18.1.11 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ , not included due to the MS settings)

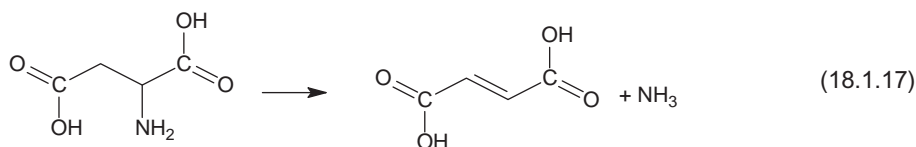
No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.26	44	124-38-9	<b>55.50</b>
2	Propene	4.61	42	115-07-1	3.09
3	2-Butene	5.18	56	624-64-6	0.39
4	1,3-Butadiene	5.38	54	106-99-0	0.71
5	Formaldehyde	5.97	44	75-07-0	0.59
6	1,3-Cyclopentadiene	8.68	66	542-92-7	0.42
7	Propanal	8.82	58	123-38-6	0.48
8	Isocyanic acid	10.71	43	75-13-6	0.05
9	Acetonitrile	11.01	41	75-05-8	2.24
10	2-Propenenitrile	12.00	53	107-13-1	3.01
11	Propanenitrile	16.30	55	107-12-0	1.07
12	Benzene	16.51	78	71-43-2	0.40
13	2-Butenenitrile	20.10	67	4786-20-3	0.31
14	Acetic acid	20.37	60	64-19-7	0.34
15	2-Methyl-2-propenenitrile	21.73	67	126-98-7	0.20
16	Butanenitrile	22.26	69	109-74-0	0.19
17	Toluene	23.18	92	108-88-3	0.22
18	Pyridine	24.06	79	110-86-1	0.42
19	2-Methylpyridine	27.11	93	109-06-8	0.19
20	Pyrrole	27.74	67	109-97-7	<b>7.40</b>
21	3-Methylpyridine	29.96	93	108-99-6	0.33
22	3-Methyl-1H-pyrrole	31.20	81	61-43-3	0.23
23	2-Methyl-1H-pyrrole	31.37	81	636-41-9	0.58
24	2-Ethenylpyridine	32.89	105	100-69-6	0.23
25	2-Ethyl-1H-pyrrole	34.60	95	1551-06-6	0.26
26	2-Ethylpyridine	36.51	107	100-71-0	0.34
27	4-Methylpyridine	36.58	93	108-89-4	0.31
28	1-Ethenyl-2-pyrrolidinone	41.55	111	88-12-0	0.41
29	2-Pyrrolidinone	42.26	85	616-45-5	<b>14.92</b>
30	4-Aminopyrimidine	42.47	95	591-54-8	1.82
31	5-Methyl-2-pyrrolidinone	43.02	88	108-27-0	0.20
32	Unknown	43.69	125	N/A	0.75
33	Unknown	45.67	135	N/A	0.29
34	Unknown	46.08	125	N/A	0.44
35	1,2,4-Triazine-3,5[2H,4H]-dione	46.24	113	461-89-2	0.32
36	1,3,4,6,7,9a-2H-Quinazoline	49.19	137	1004-90-6	0.13
37	6-Methyl-3,4-pyridinedimethanol?	50.73	153	466-11-3	0.10
38	1,5-Diazabicyclo[5.4.0]undec-5-ene	50.95	152	6674-22-2	0.46
39	5-Azabenzimidazole?	54.65	119	272-97-9	0.38
40	Unknown	71.59	196	N/A	0.30



Formation of 2,5-pyrrolidinedione (Ret. time: 42.15 min) from aspartic acid also implies no  $\text{CO}_2$  elimination, while the formation of 2-pyrrolidinone from glutamic acid takes place with  $\text{CO}_2$  elimination as shown below:



The stability of carboxyl groups in aspartic acid is high, and the group is retained even in some reactions occurring with the elimination of  $\text{NH}_3$ . This explains, for example, the formation of 2-butenedioic acid, as shown in the following reaction:



The homologous glutaconic acid (2-pentenedioic acid) is not formed in glutamic acid pyrolysis. One more difference between aspartic and glutamic acids consists of the number of pyridines detected in the pyrolysate of glutamic acid that were not present in aspartic acid pyrolysate.

Amino acids, having two functional groups, can form a salt as an acid (e.g., with cations such as  $\text{Na}^+$ ,  $\text{K}^+$ , etc.) and also a salt as a base (e.g., hydrochlorides with  $\text{HCl}$ , etc.). Glutamic acid (and aspartic acid), having two  $\text{COOH}$  groups, can form monobasic salts and dibasic salts. Two pyrograms, one for glutamic acid hydrochloride and one for glutamic acid monosodium salt, are shown in Figures 18.1.12 and 18.1.13, respectively. Pyrolysis was performed at  $900^\circ\text{C}$  in the same conditions as previously indicated for the other amino acids.

The pyrogram for L-glutamic acid hydrochloride shown in Figure 18.1.12 is very similar to that of glutamic acid shown in Figure 8.1.11. Only the peak intensities vary to some extent. Between 6.40 min to 36.07 min, the baseline in the pyrogram of L-glutamic acid hydrochloride is high due to the formation of  $\text{HCl}$ . Hydrochloric acid does not elute well from the column selected for separation and does not form a unique peak.

The peak identification from the pyrogram of glutamic acid monosodium salt is given in Table 18.1.11. Most peaks had the same identity with those from glutamic acid pyrolysate, listed in Table 18.1.10,

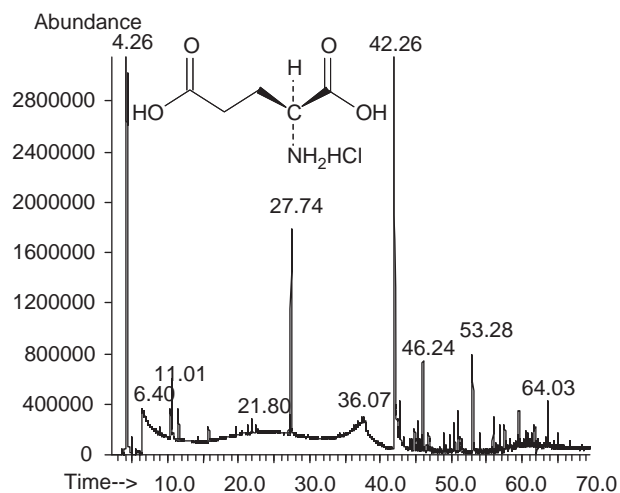
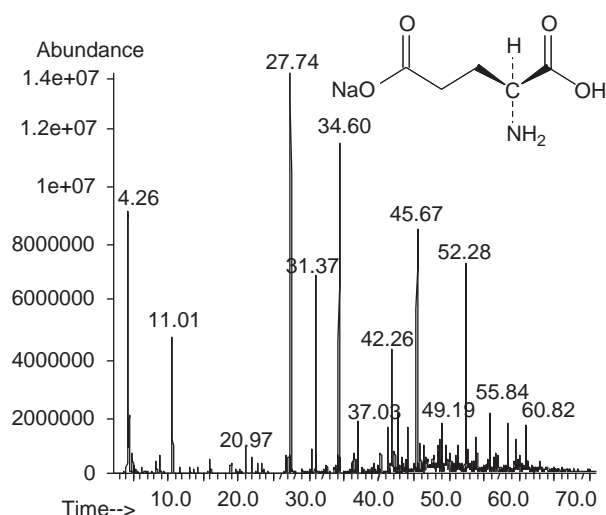


FIGURE 18.1.12. Pyrogram obtained at  $900^\circ\text{C}$  for L-glutamic acid hydrochloride.

FIGURE 18.1.13. Pyrogram obtained at 900°C for *L*-glutamic acid Na salt.TABLE 18.1.11. Peak identification as a function of retention time for the pyrogram of glutamic acid monosodium salt shown in Figure 18.1.13 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ , not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.27	44	124-38-9	<b>32.63</b>
2	Propene	4.61	42	115-07-1	3.42
3	2-Butene	5.18	56	624-64-6	0.67
4	1,3-Butadiene	5.38	54	106-99-0	0.26
5	Formaldehyde	5.97	44	75-07-0	—
6	1,3-Cyclopentadiene	8.68	66	542-92-7	0.16
7	Propanal	8.82	58	123-38-6	0.77
8	Isocyanic acid	10.71	43	75-13-6	—
9	Acetonitrile	11.01	41	75-05-8	<b>8.79</b>
10	2-Propenenitrile	12.01	53	107-13-1	0.39
11	Propanenitrile	16.30	55	107-12-0	0.67
12	Benzene	16.51	78	71-43-2	0.18
13	2-Butenenitrile	20.10	67	4786-20-3	0.21
14	Acetic Acid	20.37	60	64-19-7	—
15	Unknown*	20.97	83	N/A	0.75
16	2-Methyl-2-propenenitrile	21.73	67	126-98-7	0.47
17	Butanenitrile	22.26	69	109-74-0	—
18	Toluene	23.18	92	108-88-3	0.11
19	Pyridine	24.06	79	110-86-1	0.07
20	2-Methylpyridine	27.11	93	109-06-8	0.38
21	Cyclopentanone*	27.13	84	120-92-3	0.39
22	Pyrrole	27.74	67	109-97-7	<b>13.78</b>
23	3-Methylpyridine	29.96	93	108-99-6	0.47

(Continued)

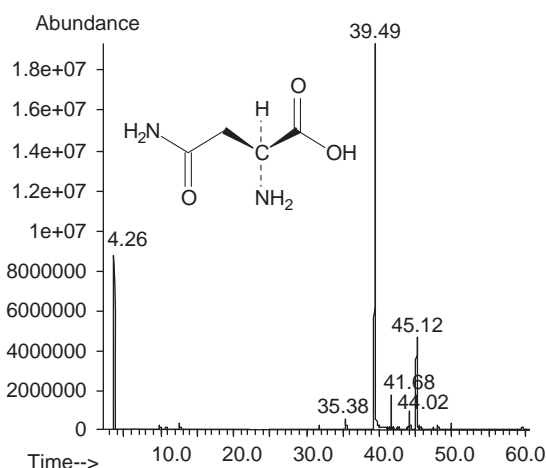
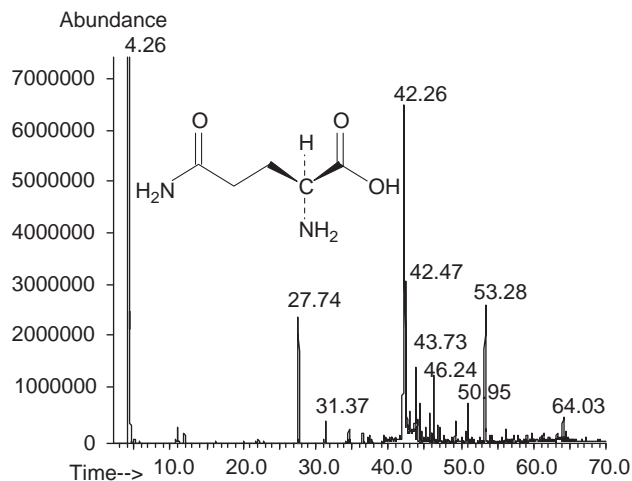
TABLE 18.1.11. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
24	3-Methyl-1H-pyrrole	31.20	81	61-43-3	0.39
25	2-Methyl-1H-pyrrole	31.37	81	636-41-9	<b>4.31</b>
26	2-Ethenylpyridine	32.89	105	100-69-6	0.05
27	2-Ethyl-1H-pyrrole	34.60	95	1551-06-6	<b>6.16</b>
28	2-Ethylpyridine	36.51	107	100-71-0	0.05
29	Aniline*	36.56	93	62-53-3	0.43
30	Benzonitrile*	36.58	103	100-47-0	0.26
31	4-Ethyl-2-methylpyrrole*	37.03	109	5690-96-0	0.38
32	4-Methylbenzamine ( <i>p</i> -toluidine)*	41.13	107	106-49-0	0.76
33	1-Ethenyl-2-pyrrolidinone	41.55	111	88-12-0	0.90
34	2-Pyrrolidinone	42.26	85	616-45-5	<b>5.53</b>
35	4-Aminopyrimidine	42.47	95	591-54-8	0.52
36	5-Methyl-2-pyrrolidinone	43.02	88	108-27-0	1.25
37	Unknown	43.69	125	N/A	—
38	Unknown	45.67	135	N/A	<b>3.24</b>
39	Unknown	46.08	125	N/A	0.01
40	1,2,4-Triazine-3,5[2H,4H]-dione	46.24	113	461-89-2	0.20
41	Indole*	48.48	117	120-72-9	0.45
42	1,3,4,6,7,9a-2H-Quinazoline	49.19	137	1004-90-6	0.84
43	6-Methyl-3,4-pyridinedimethanol?	50.73	153	466-11-3	0.32
44	4-Methyl-1H-indole*	50.90	131	16096-32-5	0.18
45	1,5-Diazabicyclo[5.4.0]undec-5-ene	50.94	152	6674-22-2	0.27
46	5-Methyl-1H-indole*	50.95	131	614-96-0	0.23
47	4,6-Dimethylpyrimidone*	51.30	124	108-79-2	0.59
48	Pyrrole-2-butyronitrile*	52.28	134	874-92-0	<b>2.97</b>
49	Pyrrole-3-butyronitrile*	52.65	134	874-91-9	0.29
50	Unknown*	53.73	148	N/A	0.50
51	1,3-Dihydro-2H-indol-2-one*	53.92	133	59-48-3	0.43
52	5-Azabenzimidazole?	54.65	119	272-97-9	0.35
53	2,3-Dihydro-1H-isindol-1-one*	56.81	133	480-91-1	0.25
54	2,3-Dihydro-5(1H)-indazolizone*	55.84	135	101733-62-0	1.02
55	Unknown*	58.32	150	N/A	0.86
56	Unknown*	59.42	152	N/A	0.55
57	1,5,6,7-Tetrahydro-4-indolone*	60.82	135	13754-86-4	0.62
58	Unknown	71.59	196	N/A	0.28

\*These compounds were not detected in glutamic acid pyrolysate.

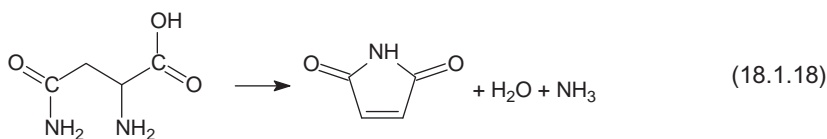
but the peak areas were significantly different. A few new compounds were seen in the pyrolysate of glutamic acid monosodium salt, and they are indicated in Table 18.1.11.

Another set of amino acids contains one additional amide group (not at the carboxyl connected to the  $\alpha$ -carbon) in their molecule. This set is represented by two homologous acids, asparagine (Asn) and glutamine (Gln). These acids are the amides formed from the carboxyl group that is not attached to the  $\alpha$ -carbon in aspartic acid and in glutamic acid, respectively. Pyrolysis of glutamine at 300 °C generates 3-pyrroline-2,5-dione, pyrrolidine-2,5-dione, piperidine-2,6-dione, pyridine-2,6-diol, pyrrolidin-2-one, and 1,5-dihydropyridine-2,6-dione, as the main pyrolysis products [9].

FIGURE 18.1.14. Pyrogram obtained at 900°C for *L*-asparagine (*MW* = 132).FIGURE 18.1.15. Pyrogram obtained at 900°C for *L*-glutamine (*MW* = 146).

For a temperature of 900°C, the pyrogram for asparagine (Asn) is shown in Figure 18.1.14 and for glutamine (Gln) is shown in Figure 18.1.15.

The pyrogram of asparagine is very similar to that of aspartic acid (see Figure 18.1.10), and the pyrogram of glutamine is very similar to that of glutamic acid (see Figure 18.1.11). Both the nature of the pyrolysis products and the peak intensities (mole percent of pyrolysate constituents) are similar for the acid and its amide. For this reason, the peak identification can be obtained for asparagine from Table 18.1.9, based on the retention times of aspartic acid, and for glutamine from Table 18.1.10, based on the retention times of glutamic acid. The explanation for similar pyrograms is that, during pyrolysis, similar reactions take place for each acid and its associated amide. The only difference between the acid and the amide is that the reaction of water elimination involving the OH from the carboxyl is replaced by NH<sub>3</sub> elimination involving the NH<sub>2</sub> from the amide group. This is shown below for the formation of 1H-pyrrole-2,5-dione from asparagine (similar to reaction 18.1.14).



The nature of the compound generating the peak at 64.03 min in the pyrogram of glutamine, which was not seen in the pyrogram of glutamic acid, was not determined. In general, the pyrolysates of asparagine and of glutamine are as dissimilar as those of aspartic acid and glutamic acid. This dissimilarity is also seen in other pyrolytic reactions where these two compounds may be involved. For example, glutamine is not known to generate 3-butenamide following the decomposition of a related Maillard type compound, while asparagine is involved in acrylamide formation (see Section 6.3).

Another set of amino acids contains an additional OH group in the molecule. This set is represented by serine (Ser), threonine (Thr), and tyrosine (Tyr). The pyrogram generated at 900 °C for serine is shown in Figure 18.1.16, and that for threonine is shown in Figure 18.1.17. The compound identifications following peak retention times for L-serine pyrolysate is given in Table 18.1.12, and for threonine pyrolysates is given in Table 18.1.13.

Serine and threonine differ only by a CH<sub>2</sub>, but serine is a primary alcohol, while threonine is a secondary alcohol. Threonine has two chiral centers, and the IUPAC name of this compound is (2S,3R)-2-amino-3-hydroxybutanoic acid. Tyrosine is *p*-hydroxyphenyl alanine and contains a phenolic group.

Pyrolysis products of serine contain as the main pyrolysis products (besides CO<sub>2</sub> and very likely NH<sub>3</sub>, which is not listed) ethyl isocyanate and 3,6-dimethylpiperazine-2,5-dione. The formation of ethyl isocyanate can be explained as resulting from 3,6-dimethyl-piperazine-2,5-dione, which is also present in the pyrolysate. The isocyanate is generated by a reaction similar to 18.1.8. The formation of

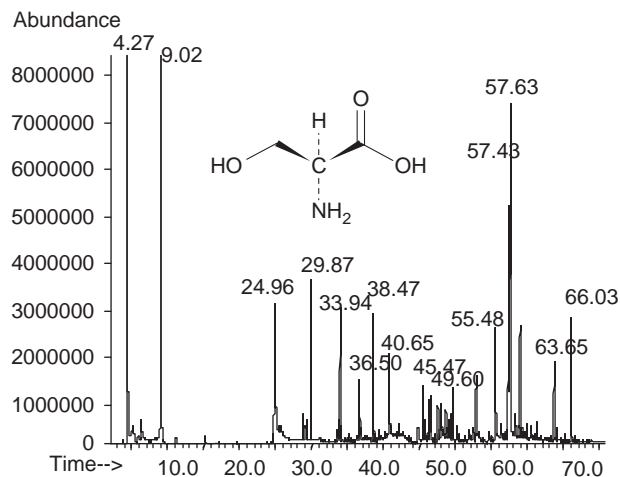


FIGURE 18.1.16. Pyrogram obtained at 900 °C for L-serine (MW = 105).

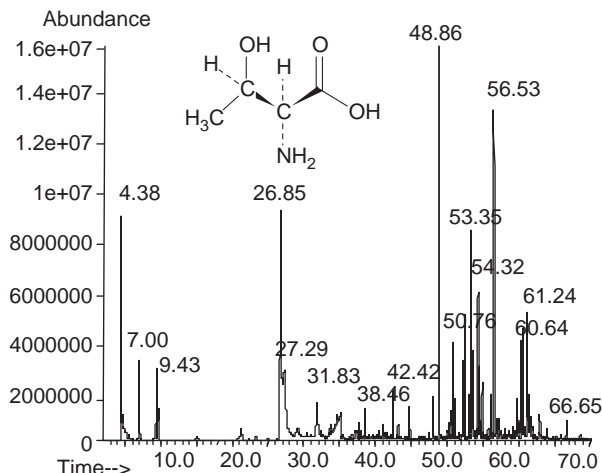
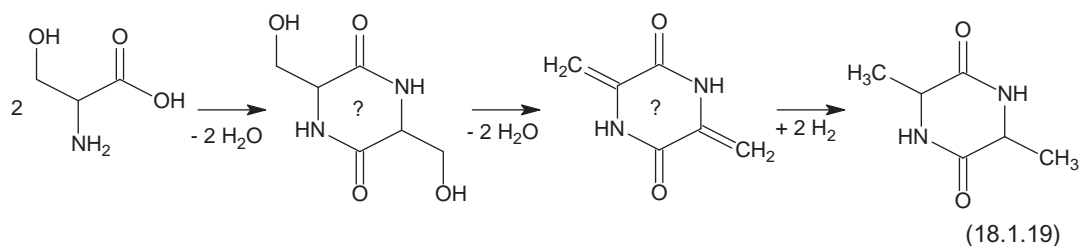


FIGURE 18.1.17. Pyrogram obtained at 900 °C for L-threonine (MW = 119).

TABLE 18.1.12. Peak identification as a function of retention time for the pyrogram of serine in Figure 18.1.16 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ , not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.27	44	124-38-9	37.91
2	Ethylamine	6.26	45	75-04-7	2.00
3	Ethyl isocyanate	9.02	71	109-90-0	<b>14.44</b>
4	Monoethanolamine	24.82	61	141-43-5	2.06
5	Pyrazine	24.96	80	290-37-9	4.59
6	2-Methylpyridine	28.72	93	109-06-8	0.49
7	3-Methylpyridine	29.18	93	108-99-6	0.28
8	Methylpyrazine	29.87	94	109-08-0	3.42
9	Ethylpyrazine	33.94	108	13925-00-3	2.28
10	2,3-Dimethylpyrazine	34.13	108	5910-89-4	0.28
11	2-Ethyl-6-methylpyrazine	36.50	122	13925-03-6	0.62
12	2,6-Diethylpyrazine	38.47	136	13067-27-1	1.16
13	2-(1-pyrrolyl)ethanol	40.65	151	N/A	1.56
14	2,4-Dimethyloxazole	44.77	97	7208-0501	0.43
15	5-Triazolo[5.1-a]pyrimidin-7(1H)-one?	45.47	136	4866-61-9	0.76
16	2-Hydroxy-3-ethylpyrazine	45.76	124	N/A	0.44
17	1-Methyl-2-pyrrolidone	46.17	99	N/A	0.25
18	1-Methyl-1H-imidazole-2-carboxaldehyde	46.34	110	13750-81-7	0.84
19	3-Ethoxypyridinamine?	46.48	138	10006-74-3	0.72
20	4-Pyridinamine in mix	47.54	94	504-24-5	0.87
21	4,5,6-Trimethyl-2-pyrimidone	47.89	138	65133-47-3	0.43
22	2-Amino-4-methyl-3-pyridinol	48.06	124	20348-18-9	0.93
23	2-Acetyl-3,4,6-trimethylpyrazine	48.65	164	125186-38-1	0.30
24	1-Aminomethyl-4,5,6,7-tetrahydrobenz-[d]isoxazole-4-one	49.38	166	N/A	0.29
25	Unknown	49.60	138	N/A	0.97
26	5-Methyl-2,4-imidazolidinedione	52.85	114	616-03-5	1.63
27	Unknown	55.48	154	N/A	2.22
28	3,6-Dimethylpiperazine-2,5-dione	57.63	142	5625-46-7	<b>13.92</b>
29	1,3-Diazepane-2,4-dione	58.93	128	75548-99-1	1.82
30	Unknown (same as from alanine)	63.65	193	N/A	0.74
31	Unknown (same as from alanine)	63.96	207	N/A	0.08
32	Unknown	66.03	194	N/A	1.25

3,6-dimethyl-piperazine-2,5-dione from serine implies a water elimination reaction, and a reduction process with an external hydrogen source that may take place as shown in the following sequence:

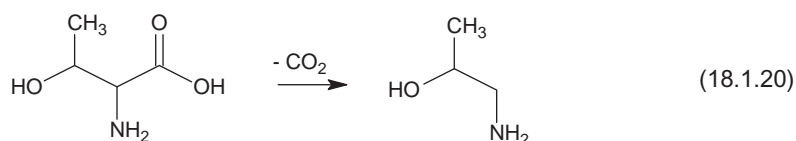


An unexpected number of pyrazines are present at lower levels in serine pyrolysate.

TABLE 18.1.13. Peak identification as a function of retention time for the pyrogram of threonine in Figure 18.1.17 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ , not included due to MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.38	44	124-38-9	19.08
2	<i>N</i> -Methylene- <i>N</i> -ethanamine	7.00	57	43729-97-1	3.94
3	Ethyl isocyanate	9.43	71	109-90-0	3.98
4	Acetone	9.66	58	67-64-1	1.49
5	Unknown	21.33	99	123-75-1	1.38
6	1-Amino-2-propanol	26.84	75	78-96-6	<b>22.38</b>
7	2-Methylperhydro-1,3-oxazine	27.29	101	31951-98-1	11.41
8	1-Methylpiperazine?	29.17	100	109-01-3	1.18
9	Unknown	31.83	100	N/A	2.83
10	1-Piperidincarboxaldehyde	35.09	113	2591-86-8	2.84
11	2-Ethyl-2,5-dimethylpyrazine	38.46	136	13360-65-1	0.40
12	3-(-2-methyl-1-pyrrolyl)propanol	42.43	139	N/A	0.74
13	3-(dimethyl-1-pyrrolyl)propanol	44.67	153	N/A	0.39
14	6-methyl-2-pyrazinylmethanol	48.01	124	N/A	0.80
15	Unknown	48.86	152	N/A	4.96
16	Unknown	50.76	178		1.08
17	6-Methoxy-3-acetamido-2-picoline?	50.95	180	52090-65-0	0.25
18	2-Oxo-1-methyl-3-isopropylpyrazine	52.25	152	78210-68-1	1.51
19	Unknown	52.56	178	N/A	1.30
20	3-Amino-4,6-dimethylpyridone	53.35	138	143708-29-6	3.11
21	1-Aminomethyl-4,5,6,7-tetrahydrobenz[d]isoxazole-4-one	53.59	166	N/A	1.29
22	Unknown	54.32	152	N/A	1.87
23	Unknown	56.53	196	N/A	4.35
24	2,5-Piperazinedione	60.35	114	106-57-0	2.85
25	1,4,6-Trimethyl-1,2,3,4-tetrahydroquinoxaline-2,3-dione	60.64	204	3/5/4951	1.34
26	Tentative 3-ethyl-6-vinylpiperazine-2,5-dione	61.24	168	N/A	2.01
27	Unknown	61.45	168	N/A	0.68
28	Tentative a piperazine-2,5-dione	62.93	166	N/A	0.56

Among the pyrolysis products of threonine, 1-amino-2-propanol is an important component. This compound results from a decarboxylation reaction as shown below:



Several minor components in the pyrolysate were difficult to identify. Also, DKP with substituents such as ethyl, vinyl, or hydroxyethyl were only tentatively identified.

The pyrolysis of serine and threonine were not found to lead to homologous products, the two amino acids undergoing pyrolysis in dissimilar ways.

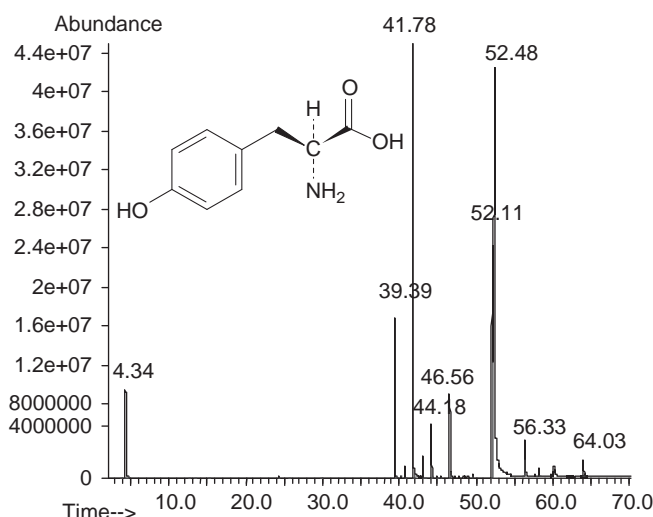


FIGURE 18.1.18. Pyrogram obtained at 900 °C for L-tyrosine (MW = 181).

TABLE 18.1.14. Peak identification as a function of retention time for the pyrogram of tyrosine shown in Figure 18.1.18 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ , not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.34	44	124-38-9	12.26
2	Toluene	24.28	92	108-88-3	0.07
3	Phenol	39.39	94	108-95-2	5.37
4	2-Methylphenol	40.79	94	95-48-7	0.31
5	4-Methylphenol	41.78	108	106-44-5	<b>19.53</b>
6	2,4-Dimethylphenol	43.09	122	105-67-9	0.51
7	4-Ethylphenol	44.19	122	123-07-9	1.39
8	2,3-Dihydrobenzofuran	46.56	120	496-16-2	3.07
9	4-(2-aminoethyl)phenol*	52.11	137	51-67-2	<b>54.17</b>
		52.48			
10	4-Hydroxybenzeneacetonitrile	56.33	133	14191-95-8	1.56
11	3-(4-hydroxyphenyl)propionitrile	58.24	147	17362-17-3	0.70
12	1H-Indole-3-ethanamine	60.15	160	61-54-1	0.83
13	A nitrile?	64.03	263	N/A	0.23

\*Both peaks at 52.11 and 52.48 min have identical mass spectra and were assigned to the same compound.

The pyrogram of tyrosine generated at 900 °C is shown in Figure 18.1.18, and the peak identification is given in Table 18.1.14. Except for the OH group in the *p*-position of the aromatic ring, L-tyrosine has a molecular structure very similar to that of phenylalanine. Pyrolysis products of tyrosine are indeed similar to those of phenylalanine. For example, among the major decomposition products of tyrosine is 5-methylphenol, which is the equivalent compound of toluene generated from phenylalanine. Also, the formation of 4-(2-aminoethyl)-phenol is similar to the formation of 2-phenylethylamine from phenylalanine. Differently from phenylalanine pyrolysate, in the case of tyrosine the pyrolysate did not contain 4-[2-(4-hydroxyphenyl)ethyl]-phenol or related compounds, which would be the equivalents of diphenylethane generated from phenylalanine.

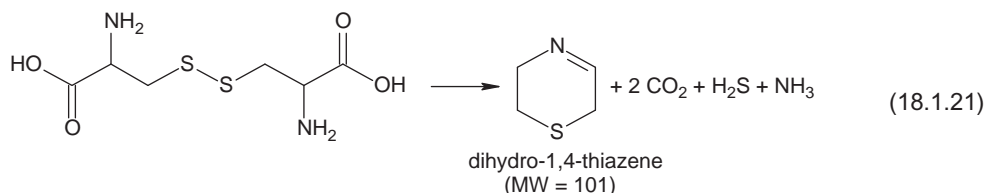
Three  $\alpha$ -amino acids contain in their molecules sulfur atoms, one in the form of an SH group (cysteine), one as a disulfide group (cystine), and another as a sulfide group (methionine). Cysteine



decomposition leads to similar compounds as cystine [17,18]. The S–S group from cystine typically decomposes with the formation of the corresponding thiols (generating cysteine) in an initial step of the process.

Pyrolysis of cystine at 900 °C generates the pyrogram shown in Figure 18.1.19. The identification of the main peaks in cystine pyrolysate is shown in Table 18.1.15. The pyrolysis products of cystine contain CO<sub>2</sub>, H<sub>2</sub>S, and a number of heterocyclic compounds containing both S and N atoms. Also, some pyridines were present in the pyrolysate.

The formation of heterocyclic compounds in cystine pyrolysis is favored by the high thermal stability of these compounds. Reactions involving CO<sub>2</sub>, H<sub>2</sub>S, and NH<sub>3</sub> eliminations are likely to take place during pyrolysis, as shown below for the formation of dihydro-1,4-thiazene:



The formation of sulfur (not detected by GC/MS) instead of H<sub>2</sub>S in a reaction similar to 18.1.21 leads to the formation of tetrahydro-1,4-thiazene.

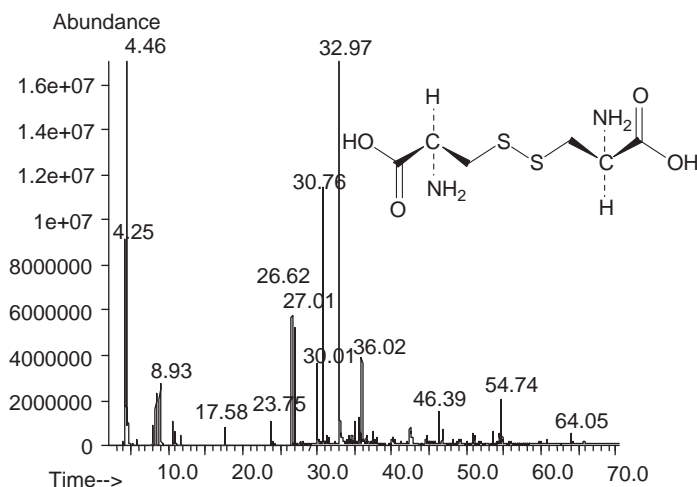


FIGURE 18.1.19. Pyrogram obtained at 900 °C for L-cystine (MW = 240).

TABLE 18.1.15. Peak identification as a function of retention time for the pyrogram of cystine shown in Figure 18.1.19 (H<sub>2</sub>, H<sub>2</sub>O, HCN, CO, NH<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub> not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.25	44	124-38-9	<b>18.25</b>
2	Hydrogen sulfide	4.47	34	7783-06-4	<b>43.30</b>
3	Ethanethiol	7.92	62	75-08-1	0.70
4	Carbon disulfide	8.39	76	75-15-0	1.91
5	Ethyl isocyanate	8.93	71	109-90-0	2.89
6	Vinyl isocyanate	10.59	69	N/A	1.44
7	Acetonitrile	10.93	41	75-05-8	1.19
8	Thiirane (ethylene sulfide)	11.73	60	420-12-2	0.46

TABLE 18.1.15. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
9	Thiophene	17.58	84	110-02-1	0.60
10	Thiazole	23.75	85	288-47-1	0.71
11	2-Methylthiazole	26.62	99	3581-87-1	2.74
12	2-Methylpyridine	27.01	93	109-06-8	2.64
13	4,5-Dihydro-2-methylthiazole	29.90	101	2346-00-1	1.34
14	4-Methylpyridine	30.02	93	108-89-4	1.76
15	Dihydro-1,4-thiazene	30.76	101	N/A	<b>5.19</b>
16	Tetrahydro-1,4-thiazene	32.97	103	N/A	<b>9.57</b>
17	5-Ethyl-2-methylthiazole	35.16	127	19961-52-5	0.33
18	Unknown	35.56	125	N/A	0.43
19	2-Ethyl-5-methylpyridine	35.73	121	18113-81-0	0.23
20	5-Ethyl-4-methylthiazole	36.02	127	31883-01-9	1.34
21	2-Isopropenylthiazole	37.49	125	13816-04-1	0.24
22	5,6-Dihydro-2,4,6-trimethyl-4H-1,3,5-dithiazine	42.46	163	638-17-5	0.86
23	Unknown	46.39	155	N/A	0.44
24	4-Phenylpyridine?	46.78	155	939-23-1	0.21
25	Unknown	50.84	183	N/A	0.12
26	Unknown	53.49	181	N/A	0.19
27	Mixture	54.49	170	N/A	0.17
28	2(1H)-quinolinone?	54.74	145	59-31-4	0.64
29	A nitrile	64.06	263	N/A	0.12

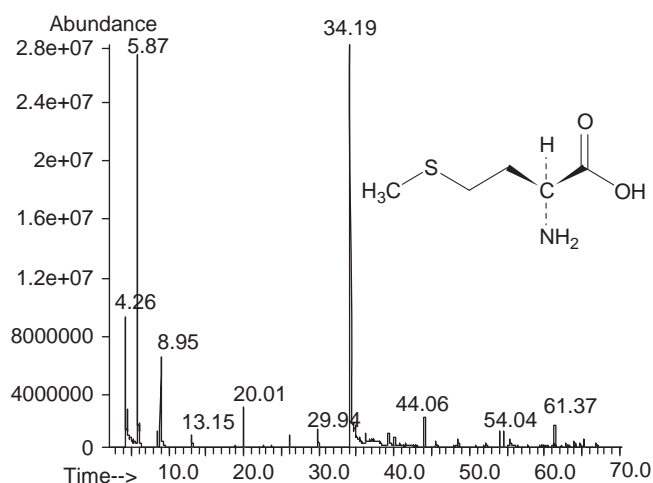


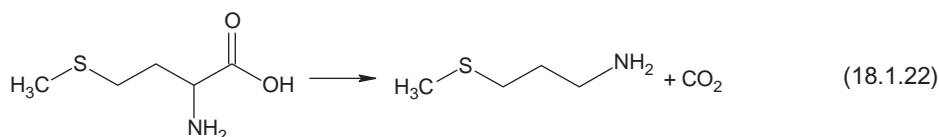
FIGURE 18.1.20. Pyrogram obtained at 900°C for L-methionine (MW = 149).

Pyrolysis of L-methionine at 900°C generates the pyrogram shown in Figure 18.1.20. The identification of the main peaks in methionine pyrolysate is shown in Table 18.1.16. The main pyrolysis products of methionine include CO<sub>2</sub>, CH<sub>3</sub>SH, 1-propenamine, and 3-methylthio-1-propanamine. The formation of methanethiol can be explained easily by the cleavage of one of the C–S bonds with the formation of two free radicals, one of them being CH<sub>3</sub>S•. This free radical generates CH<sub>3</sub>SH by hydrogen abstraction from other amino acid molecules. The main pyrolysis product,

TABLE 18.1.16. Peak identification as a function of retention time for the pyrogram of methionine shown in Figure 18.1.20 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.26	44	124-38-9	<b>14.70</b>
2	Hydrogen sulfide	4.49	34	6/4/7783	1.92
3	Methanethiol	5.88	48	74-93-1	<b>19.84</b>
4	Ethylamine	6.07	43	75-04-7	1.88
5	Dimethylsulfide	8.46	62	75-18-3	0.58
6	1-Propenamine	8.95	57	107-11-9	<b>4.94</b>
7	Methyl vinyl sulfide	13.16	74	N/A	0.49
8	3-(methylthio)-1-propene	18.82	88	10152-76-8	0.31
9	1-(methylthio)-1-propene	20.01	88	52195-40-1	1.19
10	Dimethyldisulfide	22.77	94	624-92-0	0.29
11	Tetrahydrothiophene	26.12	88	110-01-0	0.34
12	3-Methylpyridine	29.94	93	108-99-6	0.49
13	3-Methylthio-1-propanamine	34.19	105	4104-45-4	<b>51.10</b>
14	3,4-Dimethylpyridine	34.77	107	583-58-4	0.29
15	3-Thiophenethiol?	39.36	115	7774-73-4	0.27
16	Unknown	44.06	143	N/A	0.50
17	Unknown	54.04	193	N/A	0.19
18	5,6,7,8-Tetrahydroquinoline?	54.55	132	10500-57-9	0.25
19	Unknown	61.38	131	N/A	0.43

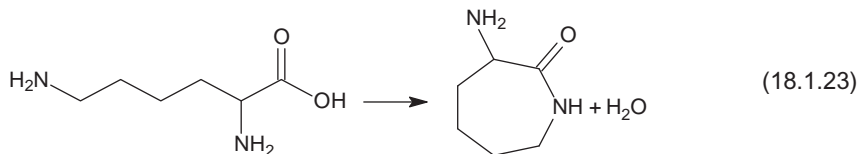
3-methylthio-1-propanamine, is generated from a decarboxylation reaction as shown below:



Other similar  $\alpha$ -amino acids are those containing an additional  $NH_2$  group in their molecule. Two acids are common in this set, lysine ( $\alpha,\epsilon$ -diaminohexanoic acid) and ornithine ( $\alpha,\delta$ -diaminopentanoic acid). However, ornithine is not involved in protein synthesis. When ornithine was artificially incorporated in a polypeptide chain, it formed a lactame interrupting the chain, which explains why polypeptide chains do not include ornithine.

The pyrogram generated at  $900^\circ\text{C}$  for lysine is shown in Figure 18.1.21 and that for L-ornithine (in HCl form) is shown in Figure 18.1.22. The identification of the main peaks in lysine pyrolysate is shown in Table 18.1.17.

The main reaction product during lysine pyrolysis is  $\alpha$ -amino- $\epsilon$ -caprolactam. The formation of this compound is shown as follows:



Reaction 18.1.23 does not account for the formation of  $CO_2$  during pyrolysis. The presence of  $CO_2$  in the pyrolysate, as indicated in Table 18.1.17, shows that other reactions (including decarboxylation) take place during pyrolysis of lysine.

Some of the peaks with higher areas in ornithine pyrolysate are identified in Table 18.1.18 as a function of their retention time.

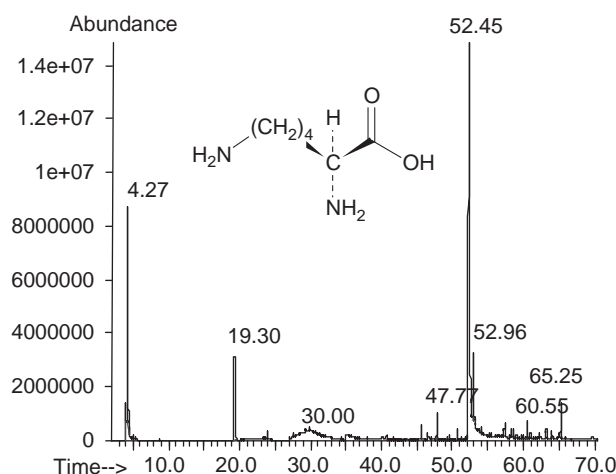


FIGURE 18.1.21. Pyrogram obtained at 900°C for L-lysine (MW = 146).

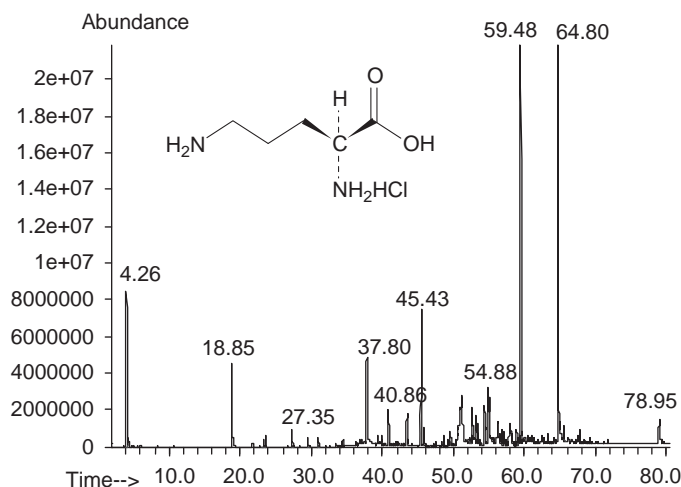


FIGURE 18.1.22. Pyrogram obtained at 900°C for L-ornithine HCl.

Pyrolysis of ornithine leads to different compounds compared to lysine. Although the pyrolysate contains 3-aminopiperidin-2-one, which is the lower homolog of  $\alpha$ -amino- $\epsilon$ -caprolactam from lysine pyrolysate, this is not the main pyrolysis product for ornithine. Two peaks, with masses 173 and 190 a.u. dominate the pyrogram, and their certain identification was not possible.

Another amino acid containing an additional nitrogenous group is arginine. Arginine contains a guanidine residue substituted in  $\delta$ -position to a pentanoic acid.

Pyrolysis of arginine HCl generates a pyrogram with numerous components. This pyrogram is shown in Figure 18.1.23. Only a small number of them were identified (some only tentatively) and are listed in Table 18.1.19. A number of heterocyclic compounds with condensed cycles were detected in arginine pyrolysate. Their formation is caused by the higher stability of these compounds at elevated temperatures.

One amino acid containing both an additional  $\text{NH}_2$  group and a secondary OH group is hydroxylysine. The pyrogram of hydroxylysine HCl is shown in Figure 18.1.24 and the identification of the main peaks is given in Table 18.1.20 as a function of retention time. Among these peaks is the one at 55.09 min

TABLE 18.1.17. Peak identification as a function of retention time for the pyrogram of lysine in Figure 18.1.21 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.27	44	124-38-9	<b>23.70</b>
2	<i>N</i> -Vinylaziridine (or isoxazole)?	21.05	69	5628-99-9	5.32
3	2,3,4,5-Tetrahydropyridine	29.68	83	505-18-0	0.63
4	2-Piperidinone	45.65	99	675-20-7	0.52
5	Hexahydro-2H-azepin-2-one ( $\epsilon$ -caprolactam)	47.77	113	105-60-2	0.76
6	3,6-Dimethyl-2-pyridinamine	50.69	122	823-61-0	0.35
7	3-Aminoazepanone ( $\alpha$ -amino- $\epsilon$ -caprolactam)	52.44	128	7929-90-7	<b>64.22</b>
8	Unknown	52.96	152	N/A	3.26
9	Mixture	57.34	178	N/A	0.40
10	Unknown	60.55	208	N/A	0.23
11	1H-Dibenzo[ <i>eg</i> ]indazole or 1H-Phenanthro[9,10- <i>d</i> ]imidazole?	65.25	218	78529-79-0 236-0202	0.62

TABLE 18.1.18. Peak identification as a function of retention time for the pyrogram of ornithine HCl shown in Figure 18.1.22 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.26	44	124-38-9	<b>13.24</b>
2	Isoxazole	18.86	69	288-14-2	<b>10.89</b>
3	2-Pyridinamine	37.80	94	504-29-0	6.88
4	3-Methylpyridinamine	40.86	108	1603-40-3	2.37
5	3-Aminopiperidin-2-one	45.43	114	N/A	<b>8.94</b>
6	Ornithine	51.07	132	70-26-8	<b>13.84</b>
7	Unknown	52.63	138	N/A	2.82
8	2-Propyl-1H-pyrrolo[2,3- <i>b</i> ]pyridine	54.41	160	1000212-02-1	0.47
9	Unknown	54.88	180	N/A	2.93
10	5H-Pyrazino[2,3- <i>b</i> ]indole?	55.04	169	1000146-98-4	1.77
11	Unknown	59.48	173	N/A	<b>13.90</b>
12	3-(2-oxo-3-1,5,6-trihydropyridin-2-one?)	64.80	190	N/A	<b>21.55</b>
13	Unknown	78.95	186	N/A	0.40

tentatively assigned to 3-amino-1H,3H,6H,7H-azepin-2-one and its mass spectrum is shown in Figure 18.1.25.

Pyrolysis of hydroxylysine generates a large number of peaks, some of medium intensity. Pyrrole and a compound tentatively identified as 3-amino-1H,3H,6H,7H-azepin-2-one are among the main pyrolysis products (together with  $CO_2$  and  $HCl$ ). The formation of 3-amino-1H,3H,6H,7H-azepin-2-one

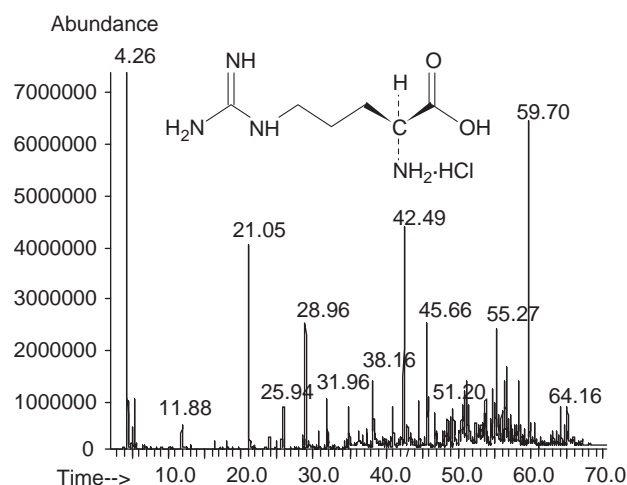


FIGURE 18.1.23. Pyrogram obtained at 900°C for *L*-arginine HCl (MW = 174+35.5).

TABLE 18.1.19. Peak identification as a function of retention time for the pyrogram of arginine HCl shown in Figure 18.1.23 ( $H_2$ ,  $H_2O$ , HCN, CO,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent*
1	Carbon dioxide	4.26	44	124-38-9	<b>41.97</b>
2	Propene	4.54	42	115-07-1	4.35
3	1,3-Butadiene	5.32	54	106-99-0	2.83
4	<i>N</i> -Vinylaziridine? (or isoxazole)	21.05	69	5628-99-9	<b>13.13</b>
5	Pyridine	25.59	79	110-86-1	2.31
6	1H-Pyrrole	28.96	67	109-97-7	4.75
7	3-Methyl-1H-pyrrole	31.96	81	616-43-3	1.86
8	3-Vinylpyridine	34.87	105	1121-55-7	1.07
9	2-Aminopyridine	38.16	94	504-29-0	1.80
10	1-Pyrrolidinecarbonitrile	42.49	96	1530-88-7	<b>6.19</b>
11	2-Methyl-5-hexenenitrile?	44.55	109	30316-00-8	1.77
12	2-Piperidinone	45.67	99	675-20-7	2.93
13	5-Methylhydantoin	50.77	114	616-03-5	1.80
14	2-Propyl-1H-pyrrolo[2,3- <i>b</i> ]pyridine	54.62	160	N/A	1.48
15	5H-Dipyrido[3,2- <i>b</i> :2',3'- <i>d'</i> ]pyrrole	55.27	169	75449-34-2	1.93
16	Unknown	56.39	179	N/A	1.83
17	Unknown	56.67	165	N/A	1.71
18	Unknown	58.25	159	N/A	1.68
19	6,7,8,9-Tetrahydro-5H-pyrazolo[2,3- <i>b</i> ]indole?	59.70	173	56015-29-3	<b>4.59</b>

\*The mole percent from Table 18.1.19 does not take into consideration the peaks that were not identified from the pyrogram.

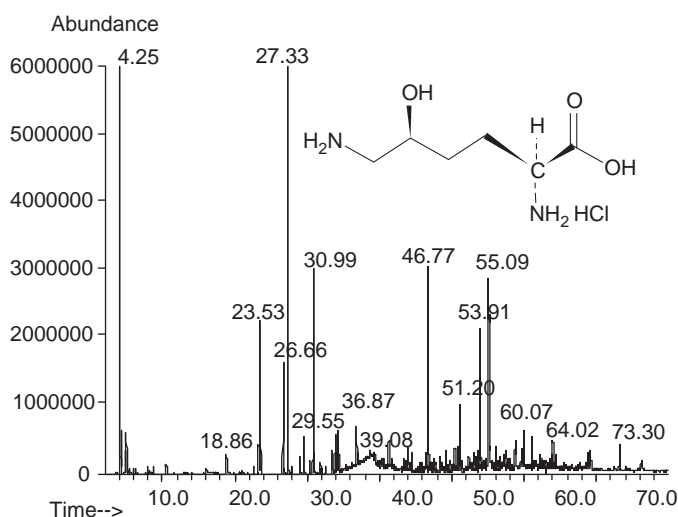


FIGURE 18.1.24. Pyrogram obtained at 900 °C for hydroxylysine hydrochloride.

is similar to the formation of 3-aminoazepanone in lysine pyrolysate. The formation of this compound is shown in the following reaction:

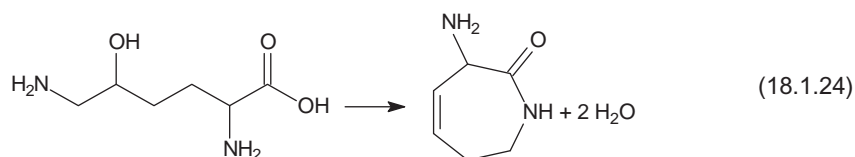


TABLE 18.1.20. Peak identification as a function of retention time for the pyrogram of hydroxylysine HCl shown in Figure 18.1.24 ( $\text{H}_2$ ,  $\text{H}_2\text{O}$ , HCN, CO,  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{N}_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.25	44	124-38-9	<b>20.26</b>
2	Propene	4.31	42	115-07-1	2.46
3	Chloromethane	4.84	50	74-87-3	0.46
4	2-Butene	4.84	56	624-64-6	0.60
5	1,3-Butadiene	5.02	54	106-99-0	1.38
6	Acetonitrile	10.58	41	75-05-8	0.82
7	1-Vinylaziridine	18.86	69	5628-99-9	0.85
8	2,3,4,5-Tetrahydropyridine	23.30	83	505-18-0	1.00
9	Pyridine	23.53	79	110-86-1	3.74
10	2-Methylpyridine	26.66	93	109-06-8	1.99
11	1H-Pyrrole	27.33	67	109-97-7	<b>13.14</b>
12	2,6-Dimethylpyridine	29.07	107	108-48-5	0.24
13	3-Methylpyrisine	29.55	93	108-99-6	0.72
14	2-Methyl-1H-pyrrole	30.82	81	636-41-9	0.49
15	3-Methyl-1H-pyrrole	30.99	81	616-43-3	3.83
16	3-Ethylpyridine	33.53	107	536-78-7	0.35
17	2,3-Dimethyl-1H-pyrrole	33.85	95	600-28-2	0.30
18	2,5-Dimethyl-1H-pyrrole	34.06	95	625-84-3	0.70

TABLE 18.1.20. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
19	2-Ethyl-1H-pyrrole	34.25	95	1551-06-0	1.15
20	3-Ethyl-1H-pyrrole	34.40	95	1551-16-2	0.35
21	2,3,5-1H-Pyrrole	36.87	109	2199-41-9	0.59
22	Hydrochloric acid	39.08	36	7647-01-0	<b>21.80</b>
23	2-Pyridincarbonitrile	41.33	104	100-70-9	0.71
24	4-Methyl-1H-indole	43.85	131	16096-32-5	0.30
25	2,5-Dimethyl-1H-indole	46.44	145	1196-79-8	0.36
26	Pyridine-2-carboxamide ( <i>a</i> -picolinamide)	46.77	122	1452-77-3	3.47
27	Caprolactam	47.52	113	105-60-2	0.19
28	Indole	48.46	117	120-72-9	0.25
29	5-Methyl-1H-pyrrole-2-carbonitrile	49.23	106	26173-92-2	0.44
30	2-Pyridinacetamide	50.46	136	3724-16-1	0.36
31	7-Methyl-1H-indole	50.93	131	933-67-5	0.37
32	2,3-Dihydro-1H-cyclopenta[ <i>b</i> ]quinoline?	51.20	170	7193-24-0	0.61
33	2,3-Dimethyl-1H-indole	53.09	145	91-55-4	0.34
34	Unknown	53.69	172	N/A	0.23
35	1-Methyl-4-ethoxy-1H-pyrazole?	53.92	126	128381-60-2	2.16
36	3-Amino-1H,3H,6H,7H-azepin-2-one	55.09	126	N/A	<b>10.94</b>
37	1-Methyl-2-(2-pyrrolidinyl)-pyrrole	56.19	150	N/A	0.26
38	Unknown	59.64	200	N/A	0.18
39	1,2,3,4,5,6,7,8-Octahydroacrydine?	60.07	187	1658-08-8	0.34
40	Unknown	61.10	201	N/A	0.31
41	2,6-Dimethylbenzo[1,2- <i>d</i> :4,5- <i>d'</i> ]bisimidazole?	63.80	186	17377-07-0	0.15
42	Unknown	64.02	180	N/A	0.28
43	2,3,5,6,7,8-Hexahydro-9-amino-1H-cyclopenta[ <i>b</i> ]quinoline?	73.30	188	62732-44-9	0.53

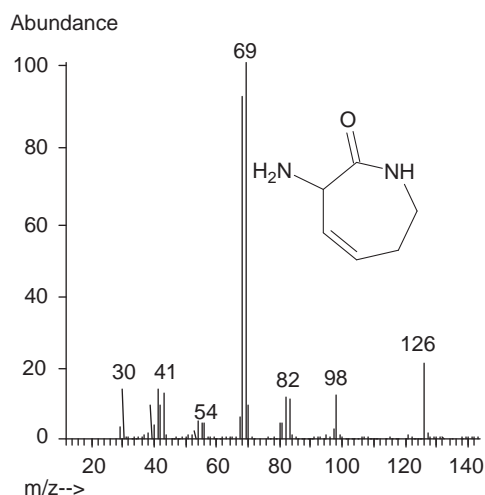


FIGURE 18.1.25. Mass spectrum tentatively assigned to 3-amino-1H,3H,6H,7H-azepin-2-one.



Another group of  $\alpha$ -amino acids present in proteins consists of those containing a heterocycle in the molecule. This group includes proline or (S)-pyrrolidin-2-carboxylic acid, hydroxyproline or (2S,4R)-4-hydroxypyrrolidin-2-carboxylic acid, histidine or 2-amino-3-(3H-imidazol-4-yl)propanoic acid or imidazol alanine, and tryptophan or (S)-2-amino-3-(1H-indol-3-yl)-propanoic acid or 1H-indole-3-alanine.

The pyrogram generated at 900 °C for proline is shown in Figure 18.1.26, and that for hydroxyproline is shown in Figure 18.1.27. The identification of the main peaks in proline pyrolysate is shown in Table 18.1.21.

The main product of proline pyrolysis is octahydro-5H,10H-dipyrrolo-[1,2-a:1'2'-d]pyrazine-5,10-dione, generated as shown in the following reaction:

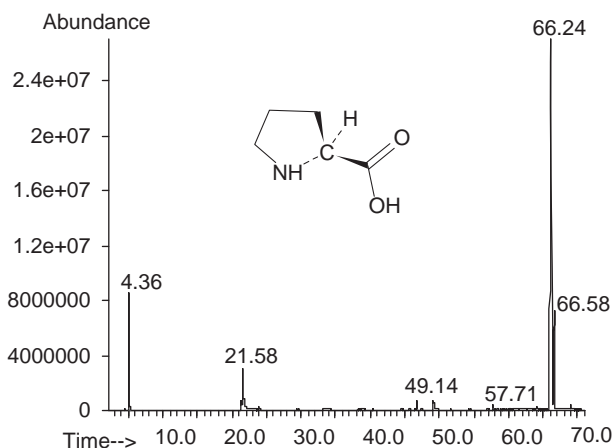
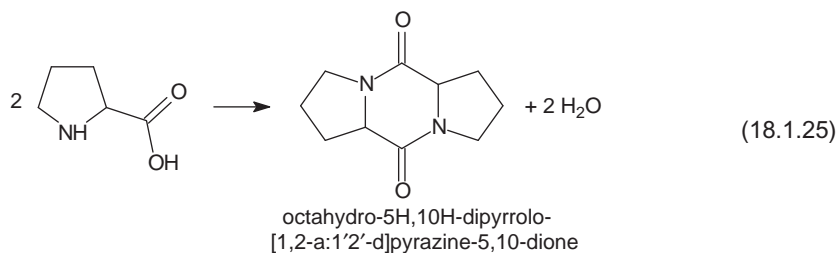


FIGURE 18.1.26. Pyrogram obtained at 900 °C for L-proline (MW = 115).

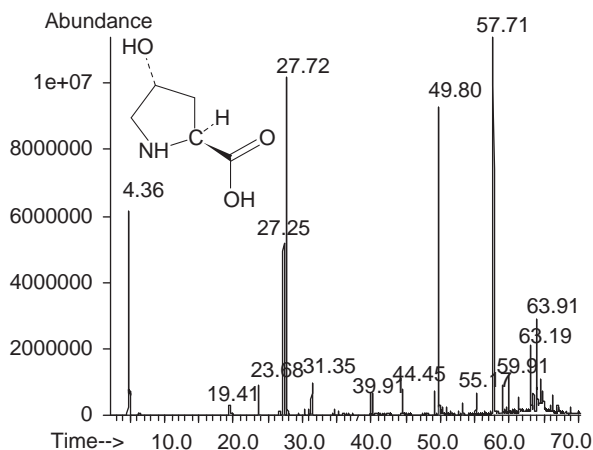


FIGURE 18.1.27. Pyrogram obtained at 900 °C for hydroxyproline (MW = 131).

TABLE 18.1.21. Peak identification as a function of retention time for the pyrogram of proline shown in Figure 18.1.26 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

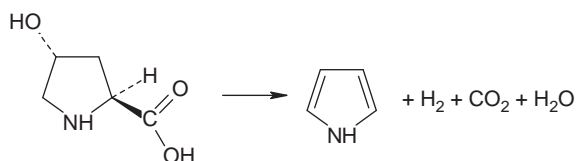
No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent*
1	Carbon dioxide	4.36	44	124-38-9	<b>19.48</b>
2	Pyrrolidine	21.21	71	123-75-1	2.78
3	<i>N</i> -Vinylaziridine? (or isoxazole)	21.59	69	5628-99-9	<b>7.75</b>
4	3,5-Diethyl-2-methylpyrazine	46.70	150	18138-05-1	0.65
5	<i>N</i> -Ethyl-cyclohexylamine?	49.14	127	5459-93-8	1.42
6	Unknown	57.71	186	N/A	0.17
7	1,7-Diazatricyclo[7.3.0.0 <sup>3,7</sup> ]dodecane-2,8-dione or octahydro-5H,10H-dipyrrolo[1,2- <i>a</i> :1'2'- <i>d'</i> ]pyrazine-5,10-dione	66.24*	194	N/A	<b>67.73</b>
		66.58			

\*The two peaks at 66.24 and 66.58 min have identical mass spectra and are assigned to the same compound.

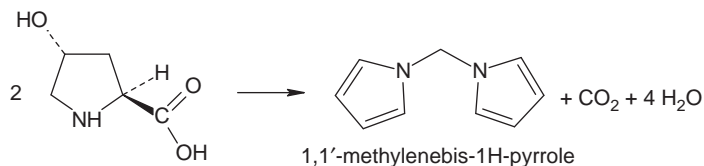
Reaction 18.1.25 does not account for the formation of  $CO_2$ , which is generated during pyrolysis. This is an indication that additional reactions, besides 18.1.25, occur during proline pyrolysis.

The identification of the main peaks in hydroxyproline pyrolysate is shown in Table 18.1.22.

Pyrolysis of hydroxyproline generates a number of compounds that are of a different type from those generated from proline. Pyrrole is a major pyrolysis product for hydroxyproline. Its formation is a result of  $CO_2$  elimination,  $H_2O$  elimination, but also of  $H_2$  elimination. Pyrrole formation from hydroxyproline is shown in the following reaction:



In proline pyrolysate, pyrrole is not detected and pyrrolidine is present only at a level of about 3%. The peak tentatively assigned to *N*-vinylaziridine in proline pyrolysate is absent in hydroxyproline pyrolysate. Also, a compound similar to 1,1'-methylenebis-1H-pyrrole or (pyrrolylmethyl)pyrrole is not found in proline pyrolysate. The formation of this compound from hydroxyproline can be explained by the following reaction:



In the formation of 1,1'-methylenebis-1H-pyrrole, besides the  $H_2O$  and  $CO_2$  elimination, oxidation/reduction reactions must participate.

A number of peaks in hydroxyproline pyrolysate were tentatively identified as related to octahydro-5H,10H-dipyrrolo-[1,2-*a*:1'2'-*d'*]pyrazine-5,10-dione (proline DKP) since they show mass spectra very

TABLE 18.1.22. Peak identification as a function of retention time for the pyrogram of hydroxyproline shown in Figure 18.1.27 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.36	44	124-38-9	<b>28.42</b>
2	1-Methyl-1H-pyrrole	23.68	81	96-54-8	1.99
3	1-Ethyl-1H-pyrrole	27.25	95	617-92-5	8.14
4	Pyrrole	27.73	67	109-97-7	<b>26.22</b>
5	3-Methyl-1H-pyrrole	31.35	81	616-43-3	1.91
6	2,3-Dihydro-1H-indole	39.91	119	496-15-1	0.72
7	5,6,7,8-Tetrahydroindolizine	40.17	121	13618-88-7	0.74
8	1,1'-Methylenebis-1H-pyrrole	49.80	146	54063-11-5	<b>10.22</b>
9	Unknown	55.17	188	N/A	0.45
10	Pyrrolo[1,2-a]pyrrolo[1,2-d]piperazine-4,8-dione?	57.71	186	N/A	<b>11.50</b>
11	Unknown	58.98	186	N/A	0.69
12	6-(2-pyridyl)pyridin-3-ol?	59.91	172	N/A	1.04
13	Unknown	63.19	190	N/A	2.02
14	Pyrrolidino[1,2-d]pyrrolo[1,2-a]piperazine-4,8-dione?	63.91	190	N/A	4.26
15	3,9-Diazatricyclo[7.3.0.0 <sup>3,7</sup> ]dodec-4-ene-2,8-dione?	64.60	192	N/A	0.77
16	2-Pyrrolino[1,5-d]pyrrolo[1,2-a]piperazine-4,8-dione?	64.95	188	N/A	0.23
17	Octahydro-5H,10H-dipyrrolo[1,2-a:1'2'-d]pyrazine-5,10-dione	66.03	194	N/A	0.12
18	Unknown	66.27	190	N/A	0.56

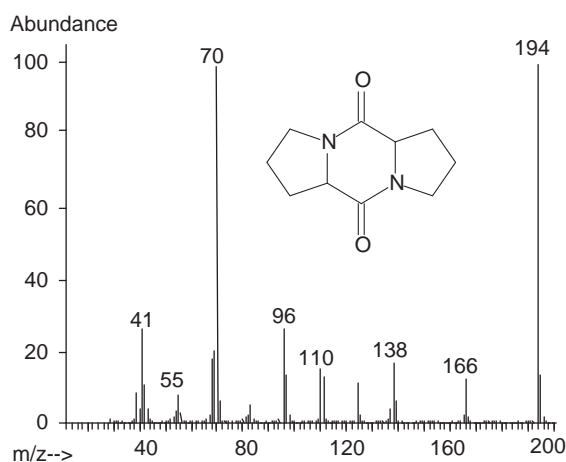


FIGURE 18.1.28. Mass spectrum of proline DKP (MW = 194).

similar to this compound (proline DKP has a mass spectrum available in Wiley 4 mass spectral library). The mass spectrum of proline DKP is shown in Figure 18.1.28 (this compound elutes as a small peak at 66.03 min in hydroxyproline pyrolysate). A peak eluting at 63.91 min in hydroxyproline pyrolysate has a similar spectrum with proline DKP, but with a number of fragments (including the molecular ion) with the

mass lower with 4 a.u. This spectrum was assigned to pyrrolidino[1,2-*d*]pyrrolo[1,2-*a*]piperazine-4,8-dione and is shown in Figure 18.1.29. Another peak eluting at 57.71 min in hydroxyproline pyrolysate also has a similar spectrum with proline DKP, but with a number of fragments (including the molecular ion) with the mass lower with 8 a.u. This spectrum was assigned to pyrrolo[1,2-*a*]pyrrolo[1,2-*d*]piperazine-4,8-dione and is shown in Figure 18.1.30.

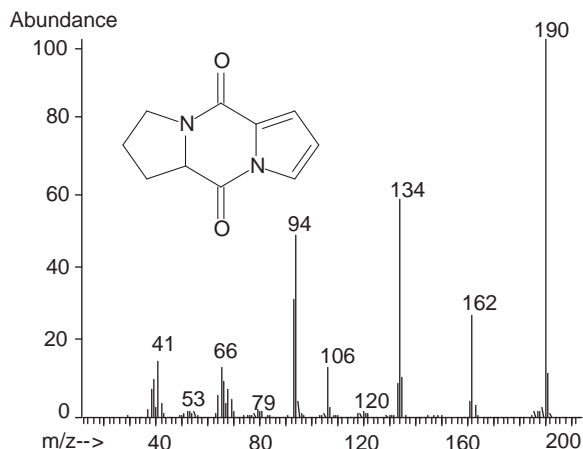


FIGURE 18.1.29. Mass spectrum assigned to pyrrolidino[1,2-*d*]pyrrolo[1,2-*a*]piperazine-4,8-dione (MW = 190).

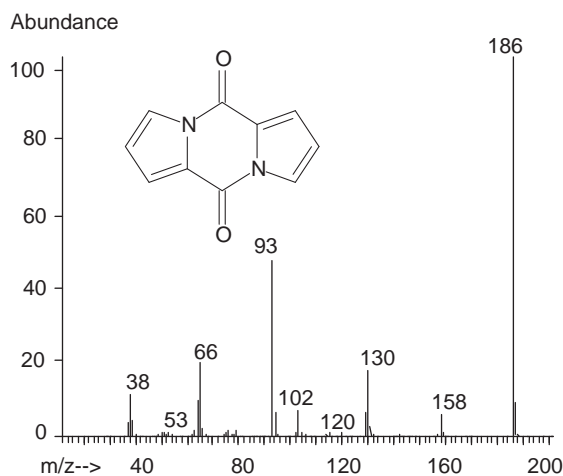
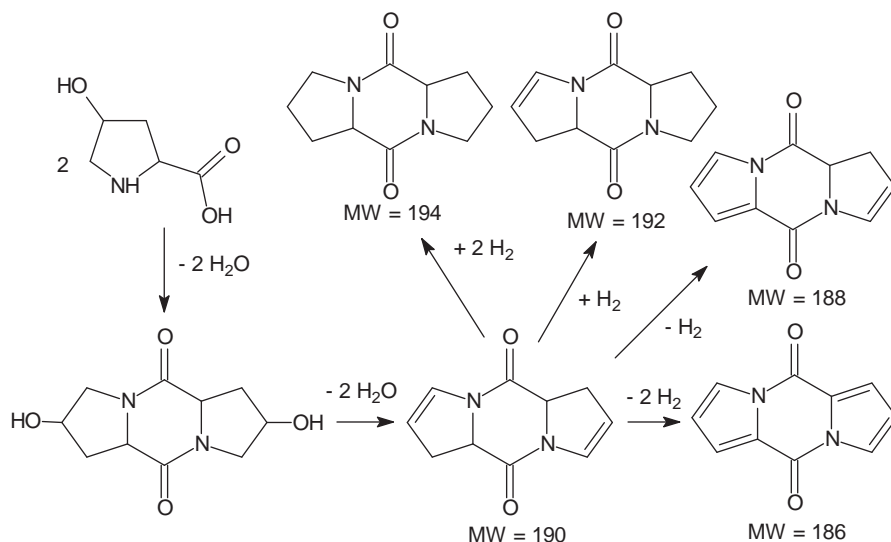


FIGURE 18.1.30. Mass spectrum assigned to pyrrolo[1,2-*a*]pyrrolo[1,2-*d*]piperazine-4,8-dione (MW = 186).

The formation of compounds with only one double bond in one of the pyrrolidine rings (yielding 3,9-diazatricyclo[7.3.0.0<sup>3,7</sup>]-dodec-4-ene-2,8-dione with MW = 192) and with a total of three double bonds in the two pyrrolidine rings (yielding 2-pyrrolino[1,5-*d*]pyrrolo[1,2-*a*]piperazine-4,8-dione with MW = 188) were also tentatively identified in hydroxyproline pyrolysate. The formation of pyrrolo[1,2-*a*]pyrrolo[1,2-*d*]piperazine-4,8-dione and of several other related compounds identified in hydroxyproline pyrolysate can be explained easily by reactions similar to the formation of proline DKP followed by the elimination

of water molecules and oxidation/reduction reactions. The scheme describing these reactions is shown below:



The pyrogram generated at 900 °C for histidine HCl is shown in Figure 18.1.31 and that for tryptophan is shown in Figure 18.1.32.

The identification of the main peaks in histidine HCl pyrolysate is shown in Table 18.1.23.

As shown in Table 18.1.23, the main peaks in histidine HCl pyrolysate are those for CO<sub>2</sub> and HCl. Several nitriles and imidazole related compounds also were detected in the pyrolysate.

The identification of the main peaks in tryptophan pyrolysate is shown in Table 18.1.24.

As shown in Table 18.1.24, indole and 3-methyl-1H-indole are the main pyrolysis products of tryptophan. 3-Ethyl-1H-indole is also present in the pyrolysate. These compounds are obviously generated from the fragmentation of tryptophan molecule with the formation of thermally stable indole

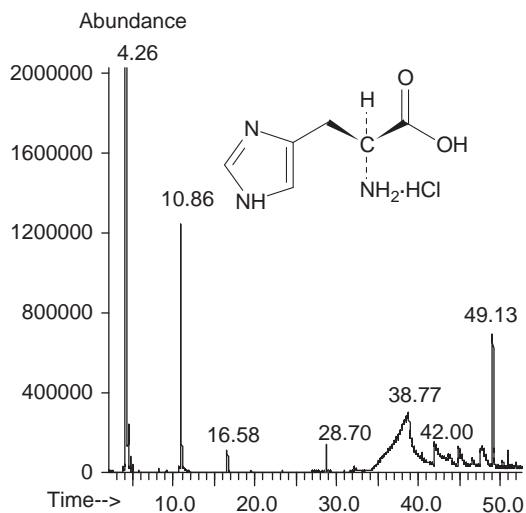


FIGURE 18.1.31. Pyrogram obtained at 900 °C for L-histidine HCl (MW = 155+35.5).

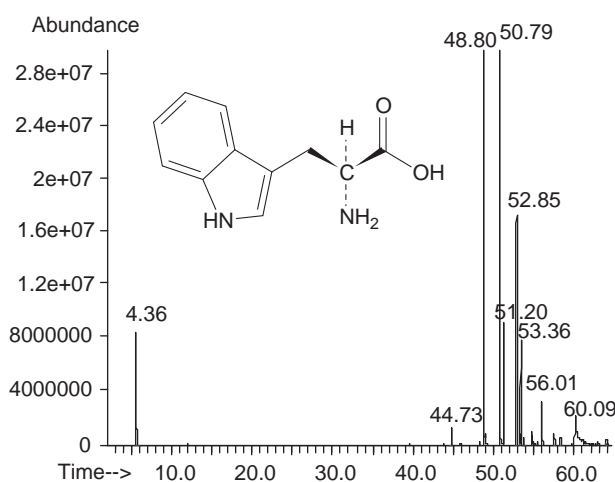
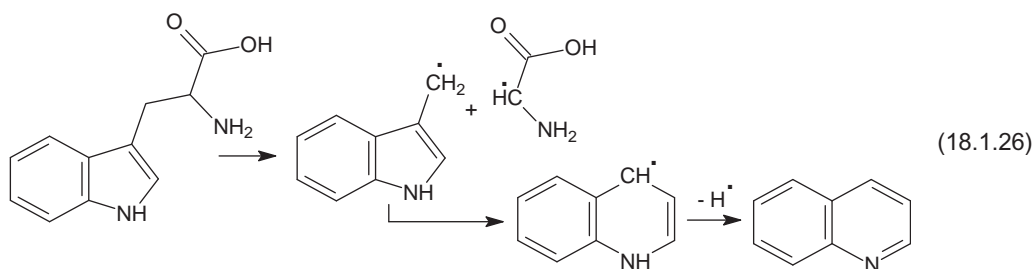


FIGURE 18.1.32. Pyrogram obtained at 900 °C for *L*-tryptophan (MW = 204).

TABLE 18.1.23. Peak identification as a function of retention time for the pyrogram of histidine HCl shown in Figure 18.1.31 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.26	44	124-38-9	<b>45.01</b>
2	Propane	4.45	44	74-98-6	1.19
3	Acetonitrile	10.86	41	75-05-8	<b>7.63</b>
4	Propanenitrile	16.59	55	107-12-0	0.58
5	1H-Pyrrole	28.71	67	109-97-7	0.51
6	Hydrochloric acid	38.78	36	7647-01-0	<b>42.61</b>
7	1H-Imidazole	42.00	68	288-32-4	0.44
8	4-Methyl-1H-imidazole	44.97	82	822-36-6	0.42
9	4-Vinylimidazole	47.84	94	3718-04-5	0.14
10	1H-Benzimidazole-5-amine	49.13	133	934-22-5	1.31
11	2-Amino-1-methyl-benzimidazole	50.90	147	1622-57-7	0.15

heterocycles. Some quinolines were also detected, their formation being explained by reactions of the following type:



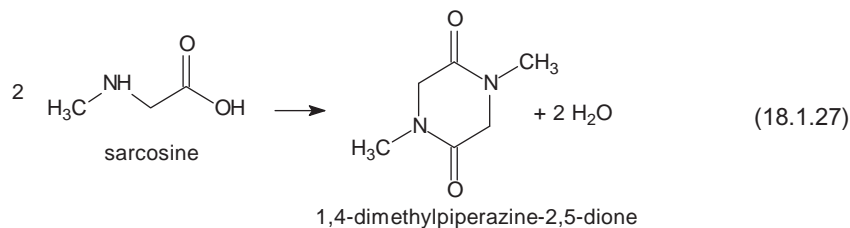
Pyrolysis of amino acids generates a variety of compounds, and there are considerable differences in the pyrolysates composition from acid to acid. Other  $\alpha$ -amino acids besides those present in proteins are known. Two such compounds are  $\alpha$ -aminoisobutyric acid (2-amino-2-methylpropanoic acid) and isovaline (2-amino-2-methylbutanoic acid), both being completely decomposed at 550 °C [19]. Another

TABLE 18.1.24. Peak identification as a function of retention time for the pyrogram of tryptophan shown in Figure 18.1.32 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

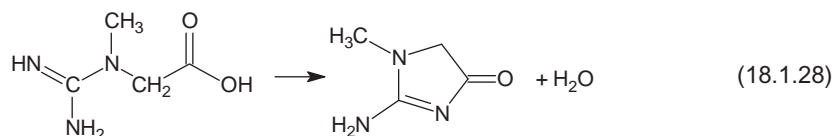
No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.36	44	124-38-9	<b>19.13</b>
2	Acetonitrile	10.98	41	75-05-8	0.24
3	2-Methylbenzeneamine (o-toluidine)	39.59	107	95-53-4	0.08
4	4-Aminostyrene	42.74	119	1520-21-4	0.04
5	2,3-Dihydro-1H-indole	43.77	119	496-15-1	0.08
6	Quinoline	44.73	129	91-22-5	0.46
7	1-Methyl-1H-indole	45.89	131	603-76-9	0.05
8	1,3-Dimethyl-1H-indole	48.23	145	875-30-9	0.10
9	Indole	48.80	117	120-72-9	<b>29.15</b>
10	4-Methylquinoline	48.91	143	491-35-0	0.48
11	3-Methyl-1H-indole	50.79	131	83-34-1	<b>35.96</b>
12	2-Methyl-1H-indole	51.20	131	95-20-5	2.70
13	3-Ethyl-1H-indole	52.85	145	N/A	<b>4.04</b>
14	2,4,6-Trimethylbenzonitrile	53.25	145	2571-52-0	0.23
15	2,3-Dimethyl-1H-indole	53.36	145	91-55-4	1.92
16	3-Methylquinoline	53.77	143	612-58-8	0.16
17	$C_3$ -1H-Indole	54.68	159	N/A	0.23
18	5,6,7-Trimethyl-1H-indole?	54.77	159	54340-99-7	0.27
19	$C_2$ -Quinoline	55.10	157	N/A	0.06
20	5,8-Dimethylquinoline	55.51	157	2623-50-9	0.06
21	7-Methylquinoline	56.01	143	612-60-2	1.10
22	<i>N</i> -Phenyl-2-pyridinamine?	57.54	170	6631-37-4	0.24
23	8-Ethylquinoline	58.31	157	19655-56-2	0.16
24	3-Ethanamine-1H-indole	60.10	160	61-54-1	2.83
25	Carbazole	62.96	167	86-74-8	0.09
26	1H-Indole-3-acetonitrile	64.81	156	771-51-7	0.14

Note:  $C_n$ -compound (e.g.  $C_3$ -1H-Indole) indicates a compound with a  $n$ -carbons alkyl substitution.

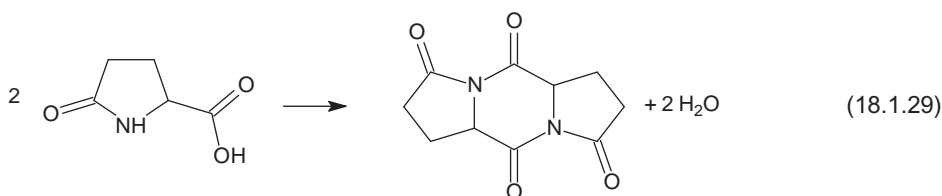
example is sarcosine, which decomposes around  $220^\circ\text{C}$  with the formation of a DKP substituted at the nitrogens with  $\text{CH}_3$  groups, as shown below [20]:



Creatine also can be considered an  $\alpha$ -amino acid. This compound, found in the muscles of all vertebrates, generates creatinine by heating at a temperature around  $170^\circ\text{C}$ , as shown in the reaction below:



Pyrolysis of pyroglutamic acid or 2-pyrrolidone-5-carboxylic acid also has been reported in the literature [1,9]. This compound is formed from glutamic acid by pyrolysis at 300 °C, together with pyrrolidinone and glutarimide. Independent pyrolysis of pyroglutamic acid leads to the formation of piperidin-2,6-dione, pyrrolidin-2-one, and low levels of a DKP as shown in the following reaction:



The generation of potentially harmful compounds from amino acid pyrolysis was the subject of various studies. The generation of HCN, for example, was evaluated by heating the amino acid at different temperatures in a sealed tube (Vycor glass tube), and the level of HCN and of NH<sub>3</sub> was measured [21,22]. The results are shown in Table 18.1.25.

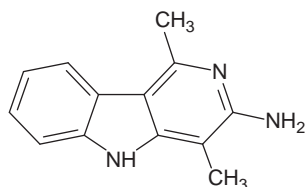
A special issue in pyrolysis of amino acids is the formation of heterocyclic amines. Some specific heterocyclic amines are mutagenic compounds, and during food processing (e.g., broiling), enough high temperatures can be reached to produce such compounds [23–28]. Some heterocyclic amines isolated

TABLE 18.1.25. The yield of HCN and of NH<sub>3</sub> generated from amino acids at different temperatures [21,22]

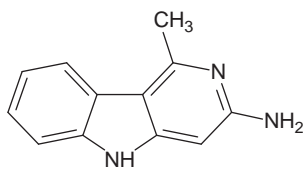
Amino acid (a.a.)	Temperature (°C)	HCN (mol/mol a.a.)	NH <sub>3</sub> (mol/mol a.a.)
Alanine	850 He	0.01	0.05
Alanine	1000	0.12	n.a.
Asparagine	1000	0.21	n.a.
Asparagine	700	0.02	n.a.
Aspartic acid	1000	0.35	n.a.
Aspartic acid	700	0.007	n.a.
Glutamic acid	850	0.33	0.01
Glutamic acid	1000	0.71	n.a.
Glutamic acid	700	0.14	n.a.
Glutamine	1000	0.46	n.a.
Glutamine	700	0.10	n.a.
Glycine	1000 He	0.32	n.a.
Isoleucine	1000	0.08	n.a.
Leucine	850	0.01	0.03
Leucine	1000	0.08	n.a.
Lysine	850	0.39	0.10
Phenylalanine	850	0.17	0.003
Phenylalanine	1000	0.43	n.a.
Proline	850	0.31	0.02
Serine	850	0.20	0.01
Serine	1000	0.45	n.a.
Tryptophan	850	0.45	0.01
Valine	850	0.03	0.05



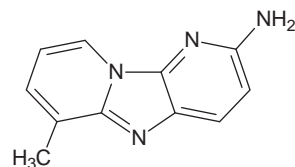
from pyrolysates performed at 550 °C from amino acids are shown as follows:



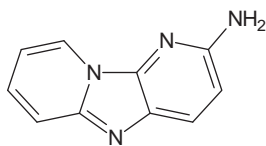
3-amino-1,4-dimethyl-5H-pyrido[4,3-b]indole  
(from tryptophan), Trp-P-1



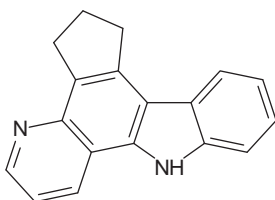
3-amino-1-methyl-5H-pyrido[4,3-b]indole  
(from tryptophan), Trp-P-2



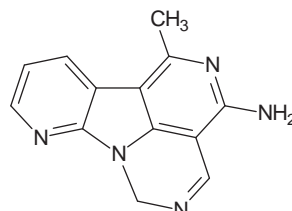
2-amino-6-methyldipyrdo-[1,2-α:3',2'-d]imidazole  
(from glutamic acid) Glu-P-1



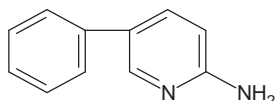
2-aminodipyrdo-[1,2-α:3',2'-d]imidazole  
(from glutamic acid), Glu-P-2



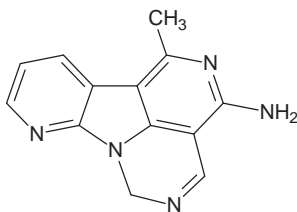
3,4-cyclopentenopyrido-[3,2-α]carbazole  
(from lysine), Lys-P-1



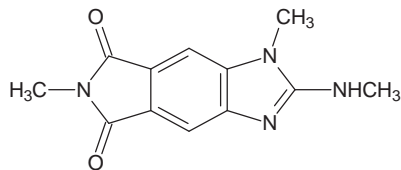
4-amino-6-methyl-1H-2,5,10,10b-tertaaza-fluoranthene  
(from ornithine), Orn-P-1



2-amino-5-phenylpyridine  
(from phenylalanine), Phe-P-1



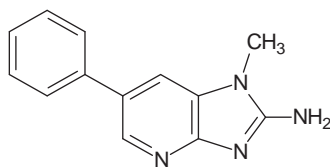
4-amino-6-methyl-1H-2,5,10,10b-tetraazafluoranthene,  
(from ornithine) Orn-P-1



4-amino-1,6-dimethyl-2-methylamino-1H,6H-pyrrolo[3,4-f]benzimidazol[2-5,7-dione],  
(from creatine) Cre-P-1

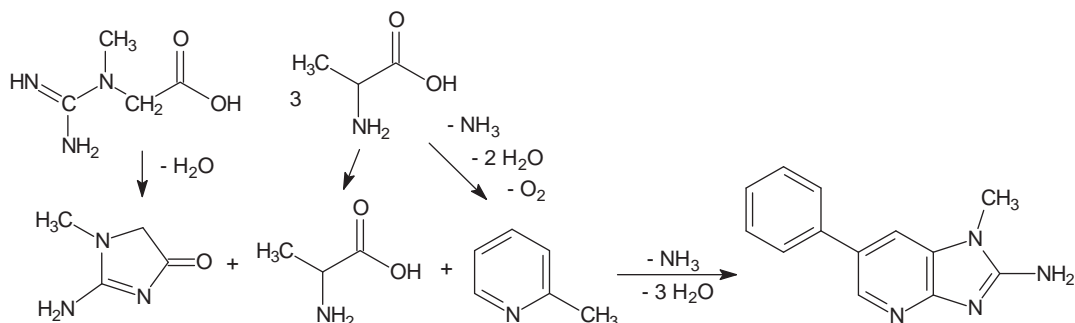
The nature of the amino acid that generated each heterocyclic amine is usually indicated in its acronym (Trp from tryptophan, Glu from glutamine, Lys from lysine, Orn from ornithine, and Cre from creatine).

Other heterocyclic amines were suspected to derive from the pyrolysis of amino acids, such as 1-methyl-6-phenylimidazo[4,5-b]pyridine-2-ylamine, which is probably generated from alanine.



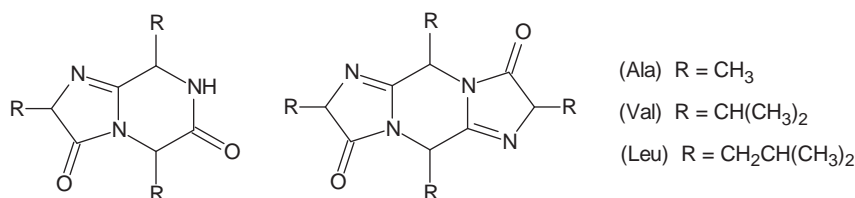
1-methyl-6-phenylimidazo[4,5-b]pyridine-2-ylamine

The mechanism of formation of heterocyclic amines from amino acid pyrolysis has been studied on several model compounds [29,30]. It was found that the interaction with sugars and creatinine from food favors the formation of heterocyclic amines [31]. A hypothetical reaction for the formation of 1-methyl-6-phenylimidazo[4,5-*b*]pyridine from creatine and alanine is shown as follows:



Since creatine is present in meat products but is absent in plants, this was considered to be an explanation for the higher propensity of heterocyclic amines formation during meat broiling and their lower level in vegetables processed at elevated temperatures.

A variety of other conditions may influence the formation of heterocyclic amines from amino acids. For example, a solid support such as silica helps the formation of heterocyclic compounds at temperatures around 500 °C, and for some amino acids even temperatures as low as 250 °C are sufficient to induce decomposition [7]. Some heterocyclic compounds generated from alanine, valine, and leucine are shown below:



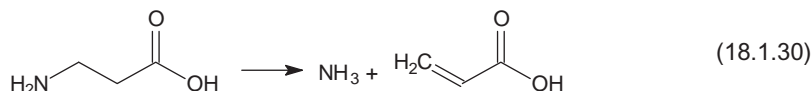
It was found also that the formation of heterocyclic amines in amino acid pyrolysates depends on the heating conditions [12,32,33]. In a study on glutamine, glutamic acid, and aspartic acid [32,34] and on asparagine and pyroglutamic acid [9], the tar and char generated from these amino acids at 300 °C and the tar and char obtained by further pyrolyzing at 625 °C the resultant from 300 °C were investigated for the formation of polycyclic aromatic hydrocarbons (PAHs) and for heterocyclic aromatic compounds. Heterocyclic compounds with one ring were detected even at temperatures as low as 300 °C, and the content in heterocyclic compounds with multiple rings increased as the temperature increased. Compounds such as quinoline, acridine, and norharman were detected in the pyrolysate of glutamic acid, and aminobiphenyl, naphthylamine, carbazole, and norharman were detected in the pyrolysate of glutamine. Aspartic acid pyrolysis also generated low levels of PAHs. The heavier heterocyclic compounds were formed mainly from the tar, and their formation was the result of condensation reactions from smaller molecules as a result of increased stability of multiple rings heterocyclic compounds at higher temperatures [29].

A number of other heterocyclic amines such as 2-amino-9H-pyrido[2,3-*b*]indole (AαC), 2-amino-3-methyl-9H-pyrido[2,3-*b*]indole (MeAαC), 2-amino-3-methylimidazo[4,5-*f*]quinoline (IQ), 2-amino-3,4-dimethylimidazo[4,5-*f*]quinoline (MeIQ), and 2-amino-3,8-dimethylimidazo[4,5-*f*]quinoxaline (MeIQx) are known to be present in the smoke generated by the pyrolysis of biological samples [35–39]. However, the source of these heterocyclic amines may not be entirely from amino acids.

**$\beta$ ,  $\gamma$ , etc. Amino acids**

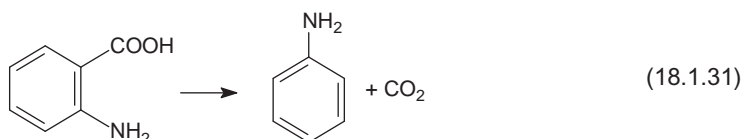
Amino acids with the COOH group and NH<sub>2</sub> group separated by one or more carbon atoms are not uncommon compounds. Examples include  $\beta$ -alanine or 3-amino-propanoic acid, which is a component of the dipeptide carnosine ( $\beta$ -alanyl-L-histidine),  $\gamma$ -aminobutyric acid (GABA), which is an inhibitory neurotransmitter in the mammalian central nervous system,  $\epsilon$ -aminocaproic acid (6-aminohexanoic acid), which is used as a pharmaceutical drug, etc. Many other amino acids from this class are known.

Limited information is available regarding the pyrolysis of these amino acids.  $\beta$ -Alanine around 210 °C decomposes generating NH<sub>3</sub> and acrylic acid as shown in the following reaction:



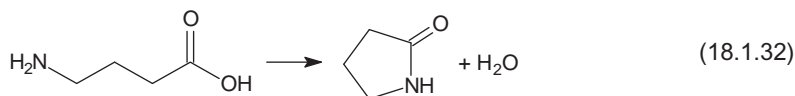
The formation of acrylic acid and ammonia is continued with the formation of acrylamide. The formation of acrylamide has an optimum temperature for its formation since acrylamide itself starts decomposing beyond 300 °C. Similar reactions with the formation of an unsaturated acid and an amine (or ammonia) also occur for other amino acids. For example, 3-(penylamino)-butanoic acid generates, by vacuum distillation, aniline and crotonic acid [40]. Pyrolysis of carnosine ( $\beta$ -alanyl-L-histidine) was found responsible for the generation of acrylamide in some bread production processes [41].

Pyrolysis of anthranilic acid (2-aminobenzoic acid), which contains the COOH and the NH<sub>2</sub> groups attached to an aromatic ring, undergoes a decarboxylation by pyrolysis, as shown below:



The decarboxylation reaction also occurs during thermal decomposition of 3-aminobenzoic acid, 4-aminobenzoic acid, and of derivatives of these acids having substituents on the aromatic ring.

Thermal decomposition of  $\gamma$ -amino acids typically leads to the formation of lactames. This reaction is shown below for GABA, which forms pyrrolidin-2-one when heated around 200 °C.



Similarly,  $\gamma$ -aminovaleric acid forms 5-methylpyrrolidin-2-one. The formation of lactames is also typical for  $\delta$ - and  $\epsilon$ -amino acids. For example,  $\delta$ -aminovaleric acid forms piperidin-2-one at 158 °C, and  $\epsilon$ -aminocaproic acid decomposes at higher temperatures primarily with the formation of  $\epsilon$ -caprolactame, although other smaller fragments as well as a polymeric material are formed in the pyrolysate. Many other amino acids are known and used for various purposes. For example, 5-aminoisophthalic acid (5-aminobenzene-1,3-dicarboxylic acid) is a compound used as a crosslinking agent in synthetic polyamides. Its pyrolysis performed in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900$  °C,  $\beta = 10$  °C/ms, THT = 10 s, and housing temperature  $T_{\text{hou}} = 280$  °C generated the pyrogram in Figure 18.1.33. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 18.1.26. Calculation of the mole percent was based solely on peak areas.

As shown in Table 18.1.26, the main pyrolysis products of 5-aminoisophthalic acid are CO<sub>2</sub>, aniline, and 3-aminobenzonitrile. In addition, a considerable number of heterocyclic compounds resulting from condensation reactions are present in the pyrolysate. The formation of aniline and CO<sub>2</sub> are the direct result of decarboxylation reactions. The formation of 3-aminobenzonitrile indicates the formation of free ammonia, which further reacts with the carboxyl groups to form amides and then nitriles. The reactions

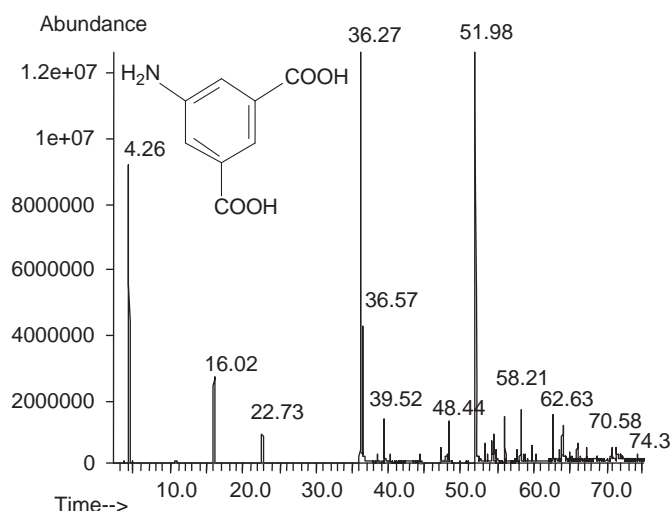


FIGURE 18.1.33. Pyrogram of 5-aminoisophthalic acid at 900 °C (MW = 181).

TABLE 18.1.26. Peak identification as a function of retention time for the pyrogram of 5-aminoisophthalic acid shown in Figure 18.1.33 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

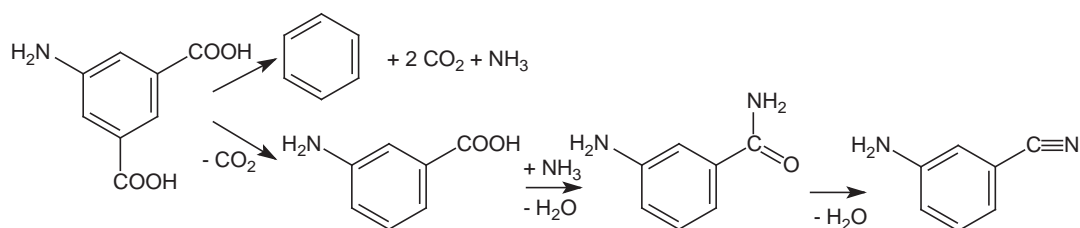
No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.26	44	124-38-9	<b>38.13</b>
2	Benzene	16.02	78	71-43-2	3.42
3	Toluene	22.73	92	108-88-3	0.73
4	Aniline	36.27	93	62-53-3	<b>24.35</b>
5	Benzonitrile	36.57	103	100-47-0	3.58
6	Phenol	38.47	94	108-95-2	0.26
7	<i>p</i> -Aminotoluene ( <i>p</i> -toluidine)	39.53	107	106-49-0	1.27
8	2-Methylbenzonitrile	40.25	117	529-19-1	0.15
9	Biphenyl	47.25	154	92-52-4	0.20
10	1H-Indazole	48.01	118	271-44-3	0.17
11	Naphthalene	48.44	128	91-20-3	0.77
12	3-Aminobenzonitrile	51.98	118	2237-30-1	<b>20.91</b>
13	Fluorene	53.44	166	86-73-7	0.21
14	4-Aminobenzylcyanide	54.25	132	3544-25-0	0.74
15	Diphenylamine	54.89	169	122-39-4	0.19
16	Phenanthridine	57.71	179	229-87-8	0.15
17	1,1'-Biphenyl-3-amine	58.21	169	2243-47-2	0.73
18	2-Phenylmethylbenzeneamine	58.54	183	28059-64-5	0.09
19	1,1'-Biphenyl-4-amine	58.83	169	92-67-1	0.10
20	Acridine	59.60	179	260-94-6	0.20
21	5H-Indeno[1,2- <i>b</i> ]pyridine	62.63	167	244-99-5	0.76
22	2-Fluorenamine	63.40	181	153-78-6	0.17
23	4-Amino-1,2-benzenedicarbonitrile	64.10	143	56765-79-8	0.88
24	1-Aminofluorene	65.03	181	6344-63-4	0.16
25	<i>N</i> -Phenyl-benzamide	65.98	197	93-98-1	0.30

(Continued)

TABLE 18.1.26. *cont'd*

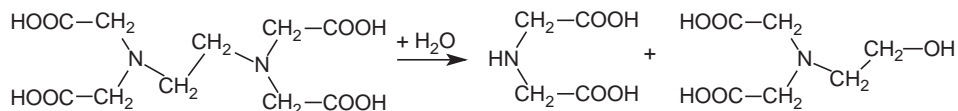
No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
26	5-Methyl-1,10-phenanthroline	67.12	194	3002-78-6	0.25
27	4-Methyl-1,10-phenanthroline?	70.58	194	31301-28-7	0.30
28	Benzidine	70.89	184	92-87-5	0.32
29	Unknown	71.51	210	N/A	0.24
30	9-Acrydinamine	74.30	194	990-45-9	0.16

leading to 3-aminobenzonitrile can be written as follows:



### Ethylenediaminetetraacetic acid and related compounds

A special group of compounds containing carboxyl and amino groups in their molecules is formed by ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), 1,2-diaminocyclohexanetetraacetic acid (DCTA), bis-2-aminoethylether-*N,N,N',N'*-tetraacetic acid (BAETA), etc. These compounds are strong chelating agents and are used to form stable combinations with many metals [42]. Thermal decomposition of the chelating agents itself is not of high interest, but the decomposition of their combinations with some metals has been studied in relation to the preparation of superconducting materials [43], nanoparticles [44], and metal oxides films [45,46]. The decomposition of EDTA starts above 260 °C with stepwise decarboxylation and H<sub>2</sub>O formation reactions. Since the compounds have an acidic character, the acidic medium during pyrolysis influences the decomposition paths. In the presence of traces of water the cleavage of N–C bond takes place with the formation of iminodiacetic acid, *N*-(2-aminoethyl)-iminodiacetic acid, and *N*-(2-hydroxyethyl)-iminodiacetic acid. This type of reaction is shown below [47]:

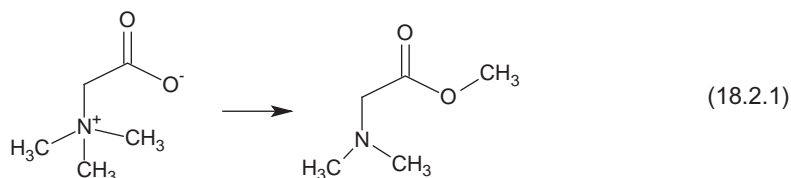


Other studies were performed on decomposition of EDTA and NTA around 260 °C in water [48].

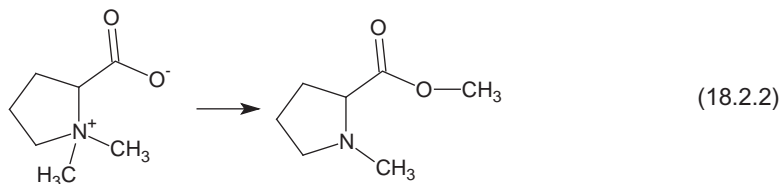
### 18.2. BETAINES

*N,N,N*-Trimethylglycine (CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>–CH<sub>2</sub>–COO<sup>–</sup> is the compound initially known as betaine. However, the term betaine is used sometimes to designate any zwitterionic compound. In this section, only the zwitterionic compounds derived from amino acids will be discussed.

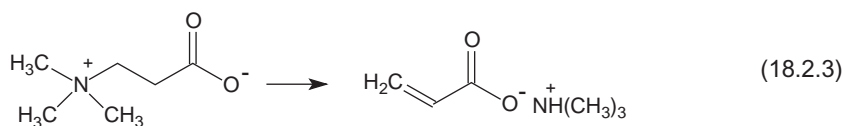
Glycine betaine undergoes at 300 °C an isomerization reaction as shown below:



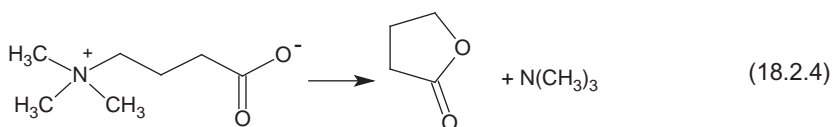
The formation of an ester at the acid group involving one of the substituents of the amino group in the betaine is a general reaction for the derivatives of  $\alpha$ -amino acids. For example, the betaine of L-proline (stachydrine) by heating at 235 °C reacts as shown below [49]:



$\beta$ -Betaines typically take a different route of thermal decomposition, generating amine salts. For example, the betaine of  $\beta$ -aminopropionic acid decomposes as shown below



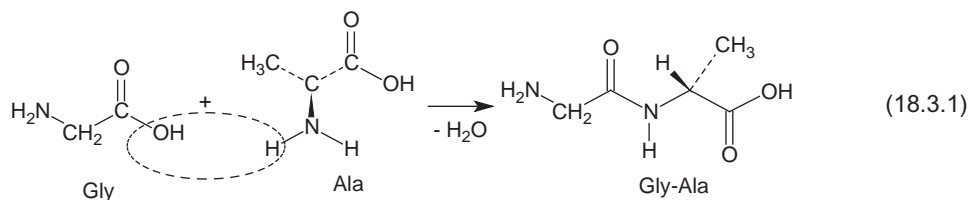
$\gamma$ -Betaines have the tendency to form lactones, as shown below for betaine of  $\gamma$ -aminobutanoic acid:



As previously shown, depending on the position of the  $\text{N}^+$  and  $\text{COO}^-$  groups, each betaine decomposes in a different manner, usually with the formation of compounds that are the most stable.

### 18.3. SMALL PEPTIDES

Peptides are short polymers formed by water elimination between  $\alpha$ -amino acid molecules. The resulting amide bond (peptide bond) is formed between the carboxyl group of one amino acid and the amino group of another amino acid. The number of amino acids participating in peptides starts with two molecules in dipeptides. Peptide nomenclature is based on the name of the amino acid components, and, for example, the dipeptide formed from two glycine molecules is glycylglycine, the one formed from a glycine and an alanine is glycylalanine, etc. It is common to indicate glycylglycine as Gly-Gly, glycylalanine as Gly-Ala etc. The formation of glycylalanine is shown below:



The compound resulting from the elimination of the OH group from the alanine and the H from the amino group of glycine is Ala-Gly (or alanylglycine).

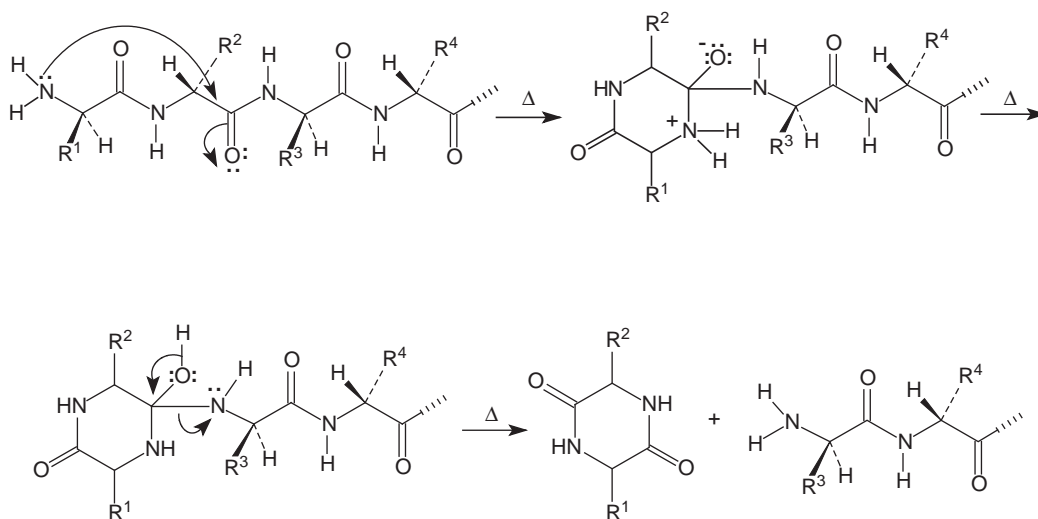
The upper limit of the number of amino acids in a peptide is not precisely defined, but it is usually accepted that it is not higher than about 50. Molecules with a higher number of amino acids are usually indicated as polypeptides or proteins. Some proteins are even formed from associations of several

polypeptides and can reach up to 10,000 amino acids. For large peptides and for proteins, the amino acid sequence (primary structure) is typically indicated with a one-letter abbreviation for the amino acids (see Table 18.1.1). The present section will discuss only the pyrolysis of small peptides made from a few amino acids. Pyrolysis of large peptides and of proteins has been discussed in various publications (see, e.g., [2]), and the subject is beyond the scope of this book.

Pyrolysis of simple peptides has been studied for various purposes, particularly for the understanding of the pyrolysis of larger peptides and of proteins [2,9,50–54]. Among the simple peptides for which pyrolysis studies have been performed are Gly-Gly [10], Gly-Gly, Gly-Pro [50,51], Val-Pro, Pro-Val, Ala-Pro, Pro-Ala, Ala-Gly, Gly-Ala [53], Phe-Leu-Met, Met-Leu-Phe, Phe-Met-Leu, Tyr-Tyr-Phe, Leu-Leu-Leu, Ala-Phe-Leu-Met, Ala-Met-Leu-Phe, Ala-Phe-Leu-Met-Tyr, Ala-Tyr-Leu-Met-Phe, Ala-Tyr-Leu-Met-Phe-Phe, Ala-Phe-Leu-Met-Tyr-Phe, Phe-Ala-Phe-Leu-Met-Tyr [53], poly-L-valine [55], etc. Peptide pyrolysis also has been proven to be useful for structure elucidation and identification of some of these compounds [56].

One type of compound generated by pyrolysis of simple peptides consists of small molecules similar to those obtained from the pyrolysis of component amino acids such as hydrocarbons (aromatic hydrocarbons from peptides containing Phe or phenols from those containing Tyr), aldehydes, pyrrole, pyrroline, indole (from peptides containing Trp), some aliphatic amines, etc.

Among the main types of pyrolysis products generated from peptides are the DKP and their secondary fragmentation products. The study of DKP formation from oligopeptides showed that the process always takes place from neighboring amino acids. The mechanism of DKP formation seems to be the following:



For dipeptides the eliminated molecule is water, for tripeptides it is an amino acid, for tetrapeptides it is a dipeptide, etc. This explains the formation of DKPs as shown in Table 18.3.1.

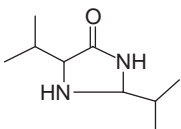
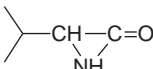
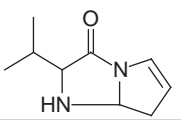
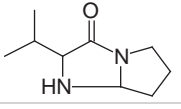
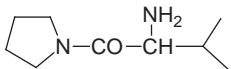
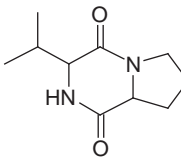
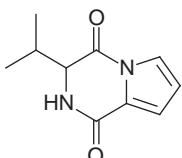
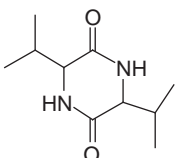
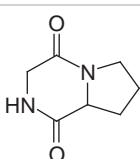
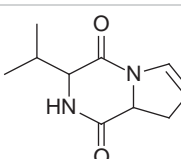
The type of DKP formed and the amount that can be detected in the pyrolysate may be influenced by the nature and stability of the R group of a particular amino acid in the peptide sequence. In addition to this, the pyrolysis conditions were found to influence the amount of DKPs. Milder pyrolytic conditions favored more DKP formation, while higher temperatures of pyrolysis generated more small molecules, as expected. The formation of DKP from peptides takes place with a higher yield than their formation from single amino acids.

The production of DKPs when one amino acid is proline leads to the formation of bicyclic compounds. As an example, several pyrolysis products for Val-Pro and Pro-Val obtained by Curie point pyrolysis at 510 °C are given in Table 18.3.2.

TABLE 18.3.1. DKP type formation noticed from different oligopeptides [56]

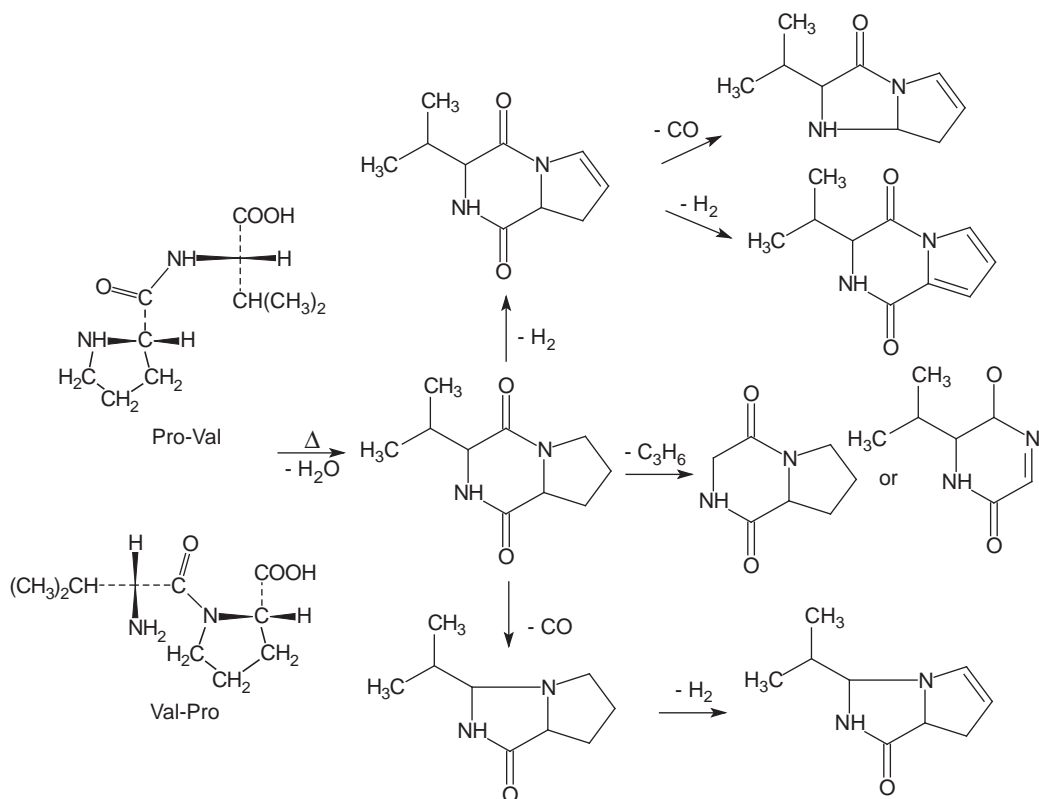
R in oligopeptide	DKP type
$R^1-R^2$	$R^1-R^2$
$R^1-R^2-R^3$	$R^1-R^2$ and smaller amount of $R^2-R^3$
$R^1-R^2-R^3-R^4$	$R^1-R^2$ and $R^3-R^4$ ( $R^2-R^3$ not observed [53])
$R^1-R^2-R^3-R^4-R^5$	$R^1-R^2$ , $R^4-R^5$ , low levels of the other in succession
$R^1-R^2-R^3-R^4-R^5-R^6$	$R^1-R^2$ , $R^5-R^6$ , low levels of the other in succession

TABLE 18.3.2. Several pyrolysis products for Val-Pro and Pro-Val

Product	MW	Product	MW
Acetone	58		170
Imidazole	68		99
Pyrroline	69	Cyanopyrrole	92
Pyrrole	67		166
Isobutyramide	87		168
	170		196
	192		198
	154		194

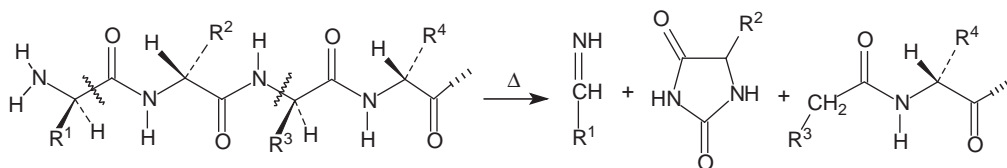


The compounds shown in Table 18.3.2 are generated by reactions of the types shown below:



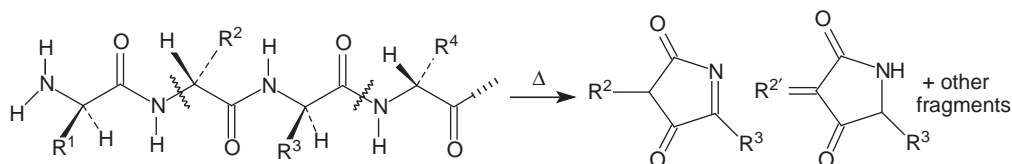
Direct pyrolysis of the DKPs corresponding to Pro-Val or Val-Pro was proven to generate the same types of compounds shown in Table 18.3.2. This is a strong indication that DKPs are among the main primary pyrolysis products of these dipeptides. However, the pyrolysis of dipeptides and their corresponding DKP does not generate identical pyrograms. Therefore, some other processes may take place during the pyrolysis of each compound.

An alternative route for dipeptide pyrolysis may be the formation of substituted imidazoliniones in reactions similar to the following:

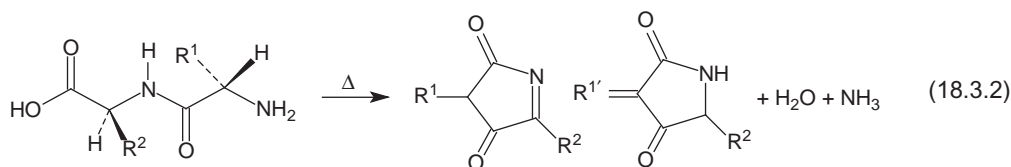


The formation of imidazolidinediones was not confirmed as coming from further thermal decomposition of DKP [50].

Besides substituted DKP and imidazolidinediones, it was proposed that disubstituted pyrrolidinediones are formed in peptide pyrolysis [2]. The reaction was presumed to take place as follows:



For the case of a dipeptide, the reaction takes place with the elimination of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  as shown below:



In reaction 18.3.2, the formation of two series of compounds is proposed because in the chromatographic separations of polypeptide pyrolysates, an additional peak is noticed for each 3-alkenyl-5-alkyl-pyrrolidin-2,4-dione. This second peak is assigned to the corresponding 2,4-dialkyl-3,5-diketopyrroline (position isomers are not possible when  $\text{R}^1$  and  $\text{R}^2$  are identical) [57].

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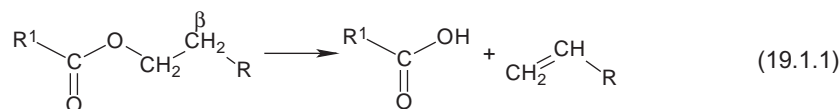
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## CHAPTER 19

*Pyrolysis of Various Derivatives of Carboxylic Acids***19.1. ORGANIC ACID ESTERS****General aspects**

Organic esters are derivatives of organic acids  $R^1\text{--COOH}$  in which the  $\text{--OH}$  group from the acid is replaced by an alkoxy or phenoxy group  $\text{--OR}^2$  (sometimes phenoxy group is specified as  $\text{--OAr}$ ). However, the formula for esters is frequently indicated as  $R^1\text{COO--R}^2$  (and not by the correct  $R^1\text{CO--OR}^2$ ) where the radical  $R^1$  is from the acid and  $R^2$  from the alcohol. The ester name is made from that of the radical  $R^2$  of the alcohol (or phenol) and the carboxylate name (name of  $R^1\text{COO}^-$ ). As an example, the ester of butyric acid with ethanol,  $\text{C}_3\text{H}_7\text{COO--C}_2\text{H}_5$ , is ethyl butyrate. The naming can also be done with full specification of the acid name and alcohol radical plus the word "ester," such as butyric acid ethyl ester for  $\text{C}_3\text{H}_7\text{COO--C}_2\text{H}_5$ .

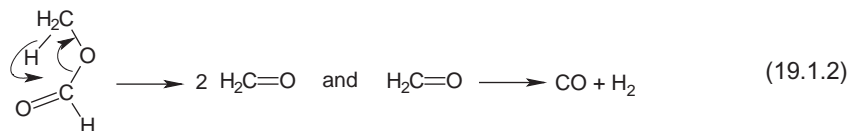
Typical reaction for the pyrolysis of esters that contain a hydrogen at the  $\beta$ -carbon in the  $R^2$  group from the alcohol moiety is the formation of an acid and an alkene as shown below:



The reaction takes place by an  $E_i$  concerted mechanism, as discussed in Section 2.2. The esters of alcohols that do not have a  $\beta$ -hydrogen in the alcohol moiety decompose differently under the influence of heat.

**Esters of alcohols that do not have a  $\beta$ -hydrogen**

Pyrolysis of methyl esters cannot occur following reaction 19.1.1 since there is no  $\beta$ -hydrogen available. Methyl formate (formate), for example, generates by pyrolysis a mixture of gases (53% CO, 43.1%  $\text{H}_2$ , 1.5%  $\text{CH}_4$ , 1.8%  $\text{CO}_2$ , and 0.6% HCHO) and liquids ( $\text{H}_2\text{O}$  and HCHO dissolved). The main reaction probably takes place as follows:



Typical for methyl esters, methyl acetate decomposes at higher temperatures than acetates of alcohols containing hydrogen atoms at the  $\beta$ -carbon (such as ethyl acetate). The decomposition of methyl acetate takes place with the formation of  $\text{H}_2$ ,  $\text{CH}_4$ , CO,  $\text{H}_2\text{O}$ , and low levels of ethylene, acetic acid, acetaldehyde, formaldehyde, etc.

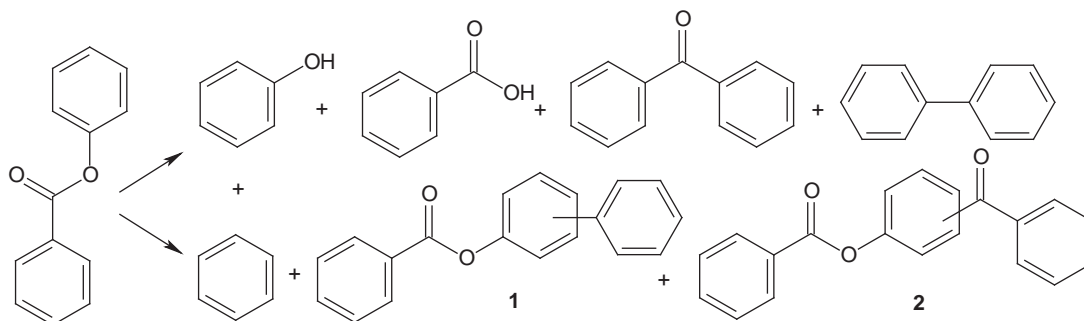
Methyl benzoate is also stable to temperatures as high as  $400\text{--}500^\circ\text{C}$ . At even higher temperatures it decomposes, generating a number of fragment molecules including benzene, biphenyl, and some larger molecules such as 4-methylphenyl benzoate.

Similarly, numerous fragments are generated by pyrolysis of methyl phthalate [1]. The decomposition of this compound starts when heated at 405 °C, but this decomposition is not advanced and increases at 608 °C to about 36%, and at 805 °C to 97%. The decomposition at 405 °C generates formaldehyde, water, phthalic anhydride (28%), and other compounds. At 608 °C the level of phthalic anhydride decreases to 3.4%, and other compounds are formed such as benzene (2.7%), toluene (5.6%), xylene (3.7%), methyl benzoate (37.3%), and other unidentified compounds. At 805 °C, the benzene level increases to 16.3%, and also that of biphenyl and small molecules such as CO<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub> increase to some extent.

Other cases where a multitude of fragments are formed from the ester pyrolysis include benzyl esters (no β-hydrogen at the alcohol). Benzyl acetate decomposes around 360 °C with the formation of toluene, methanol, CO<sub>2</sub>, CO, and low levels of CH<sub>4</sub>. Benzyl benzoate also decomposes with fragmentation, generating at 350 °C with 2 h heating a mixture containing about 50% unchanged ester plus toluene, benzaldehyde, benzoic acid, benzoic acid anhydride, and tar [2].

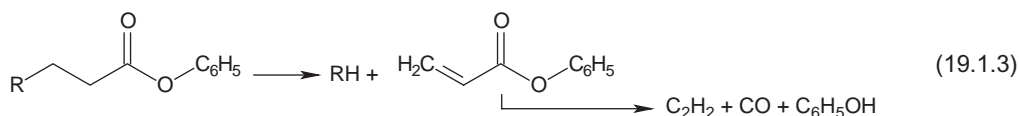
Benzyl oxalates were also studied regarding their pyrolysis products. Benzyl oxalate and oxalates with the benzyl group having additional substituents such as *p*-chloro generate by pyrolysis with good yields bibenzyl or the corresponding substituted compound [3].

Phenyl esters also have no β-hydrogen at the hydroxylic moiety (a phenol). When phenyl benzoate is heated around 400 °C from 1 h to 4 h, it generates various fragments as shown in the following scheme:



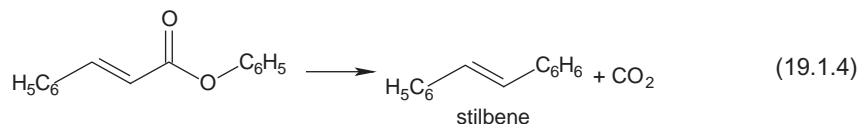
The composition of the pyrolysate varies with the heating time, generating benzene between 4.5% and 7.5%, phenol between 54.2% and 48.5%, biphenyl between 2.2% and 1.4%, benzoic acid between 27.7% and 4.2%, benzophenone between 0.0% and 5.5%, (1) between 3.6% and 7.5%, and (2) between 4.2% and 3.6% (first number indicates the level for 1 h heating time and the second for 4 h) [4].

When the hydrocarbon radical in the acid moiety contains β-hydrogens, it is possible to see the fragmentation of the acid chain, usually (but not necessarily) with further decomposition of the ester of acrylic acid generated in the reaction. One example of this type of decomposition is the pyrolysis of phenyl palmitate, which takes place around 320 °C. The reaction occurs following the general scheme indicated below:

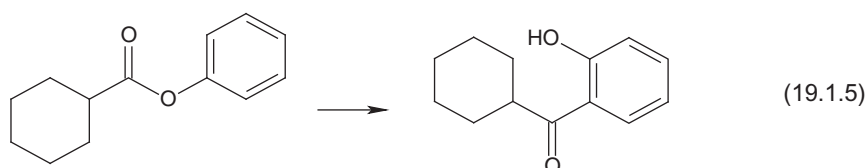


Phenyl stearate and phenyl laurate behave in a similar manner. However, this reaction is less general compared to reaction 19.1.1 for esters with β-hydrogen in the alcohol moiety. For example, when the β-hydrogen from the acid chain participates in a double bond, the reaction does not lead to an

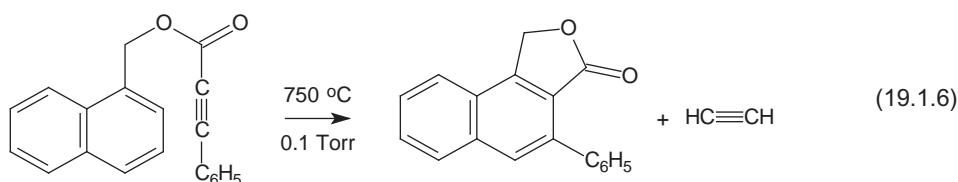
acetylenic acid. Phenyl cinnamate decomposes as shown in the following reaction [2]:



Also, when the  $\beta$ -hydrogen in the acid moiety is part of a cycle (and no  $\beta$ -hydrogen is available in the alcohol), the reaction takes a different route, as shown below for phenyl cyclohexanecarboxylate:



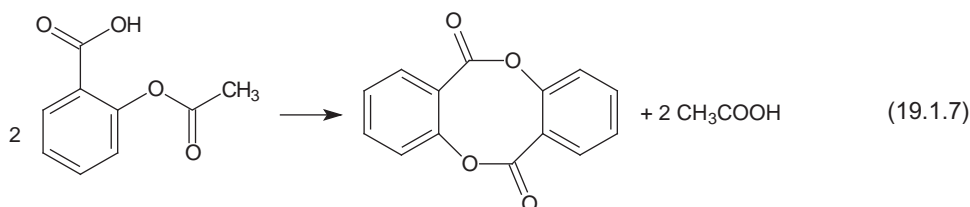
In other cases where no  $\beta$ -hydrogen to the ester group is available either in the alcohol moiety or in the acid hydrocarbon chain, the decomposition of esters takes various and sometimes unexpected routes. One example is shown in the following reaction [5]:



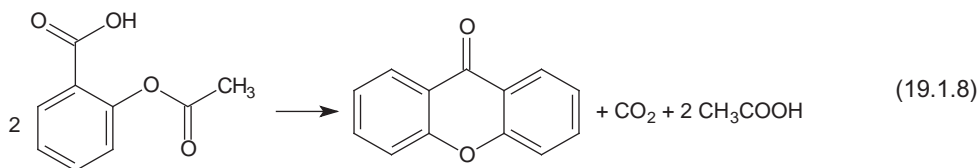
In this reaction, the mechanism seems to be a Diels–Alder condensation of the triple bond with bonds from naphthyl ring acting as a diene, followed by  $\text{C}_2\text{H}_2$  elimination. In this process, the lactone cycle remains unaffected.

### Esters with additional functional groups and no $\beta$ -hydrogen

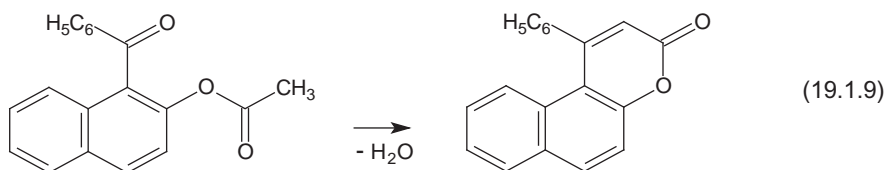
The pyrolysis route may be influenced by the existence of additional functional groups in the ester molecule. For example, the presence of a free carboxyl group can influence the pyrolysis of esters. Acetylsalicylic acid (aspirin) decomposes at melting temperature (around  $136^\circ\text{C}$ ) to generate acetic acid, salicylic acid, and di-, tri-, tetra-, etc., salicylides  $(\text{C}_7\text{H}_4\text{O}_2)_x$ . The formation of a disalicylide is shown in the following reaction:



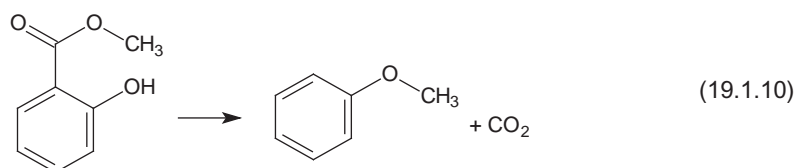
At higher temperatures aspirin generates  $\text{CO}_2$  and xanthone (40% yield), as shown in the following reaction:



The presence of a ketone group in the molecule also influences thermal decomposition. As an example, pyrolysis of  $\beta$ -( $\alpha$ -benzoyl)-naphthyl acetate takes place as shown in the following reaction [6]:

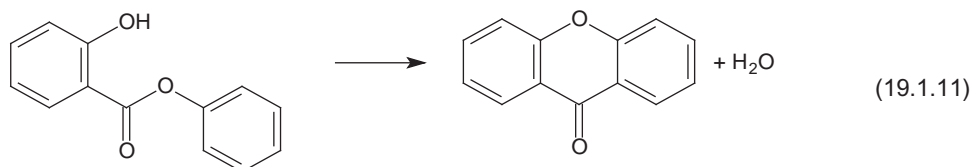


Another group that may influence the pyrolysis of the ester is the OH group. For example, methyl salicylate decomposes when heated for 2 h at 340–350 °C to generate anisole with (60–70% yield) as shown in the following reaction:



The ethyl salicylate generates ethoxybenzene (phenetole) by thermal decomposition [2]. The methyl ether of methyl salicylate is relatively stable to heating. Heated for 4 h at 400–430 °C, it does not decompose.

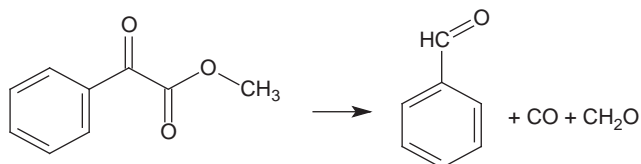
Other esters of salicylic acid can be used for the preparation of xanthenes in a reaction as shown below:



Besides the xanthone other molecules are formed in the pyrolysate, with the main constituent being phenol. Several substituted xanthenes were obtained by reactions similar to 19.1.11 [2].

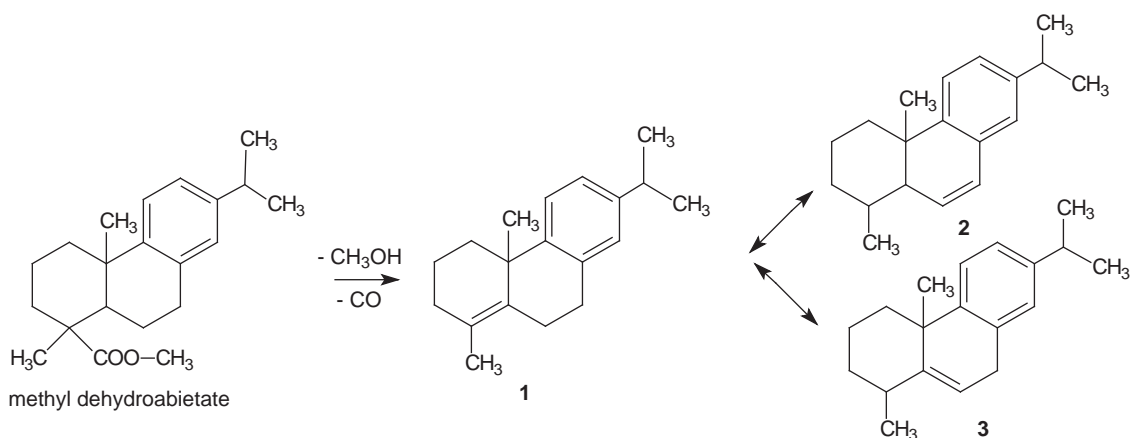
Other esters may have peculiar decomposition routes. For example, triphenylmethyl acetate by pyrolysis generates triphenylmethane. Other esters decompose with more fragments. For example,

methyl benzoylformate around 600 °C decomposes by the following reaction:

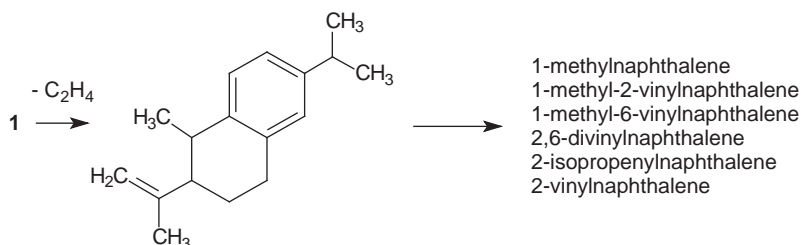


Kinetic parameters for this reaction have been established and are reported in the literature [7].

Larger ester molecules with no  $\beta$ -hydrogen available may decompose affecting the whole molecule. One example is the pyrolysis of methyl dehydroabietate. This compound was decomposed at temperatures between 600 °C and 800 °C in a vertical reactor on Vycor glass in a nitrogen flow. The pyrolysis generated numerous compounds including single-ring and multiple-ring aromatic hydrocarbons [8]. The initial reaction (similar to reaction 19.1.3) involved in this decomposition is shown below, being followed by some isomerization reactions:



Each of the intermediate reaction products 1–3 further generated a multitude of fragment molecules. As an example, from 1 several substituted naphthalenes were generated:



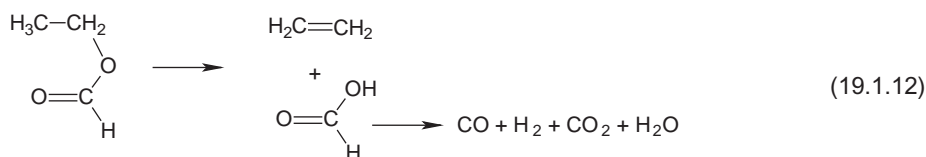
Besides naphthalene and substituted naphthalenes, among the pyrolysis products of methyl dehydroabietate were detected PAHs such as acenaphthene, acenaphthylene, phenanthrene, and methylphenanthrene. Heavier PAHs were possibly present in the pyrolysate, but their level was too low for detection.



### Esters of alcohols with $\beta$ -hydrogen and simple monocarboxylic acids

The esters of alcohols with  $\beta$ -hydrogen typically decompose following reaction 19.1.1. In general, this thermal decomposition is a "clean" reaction in the sense that it generates mainly the acid and the alkene. For this reason, the reaction has been used for synthetic purposes of olefins, particularly of those that are not sensitive to acid-catalyzed rearrangements [9]. An additional advantage of this reaction is that it can be performed in relatively mild conditions and takes place with a concerted mechanism, therefore not involving the formation of free radicals, which are associated with multiple pyrolysis products.

Ethyl formate (formiate) starts decomposing around 300 °C with the formation of ethylene,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  as the main decomposition products, and lower levels of formaldehyde. The main reaction, indicated below, follows the decomposition described by reaction 19.1.1, although the  $\text{HCOOH}$  generated in the reaction further decomposes (see reactions 17.1.1 and 17.1.2 for formic acid decomposition):



The reaction kinetics for ethyl formate has been studied both theoretically [10,11] and experimentally [12,13]. Two slightly different expressions were derived for Arrhenius equation of the first order decomposition reaction of ethyl formate. In the first expression  $A = 2.13 \times 10^{11} \text{ (s}^{-1}\text{)}$  and  $E^\ddagger = 44140 \pm 200 \text{ (cal)}$  [12], and in the other  $A = 2.19 \times 10^{12} \text{ (s}^{-1}\text{)}$  and  $E^\ddagger = 48100 \pm 500 \text{ (cal)}$  [13]. The graph showing the decomposition mole percent of ethyl formate as a function of temperature for 1.0 s exposure to the specified temperature is given in Figure 19.1.1.

Experimental data show, however, that the yield of ethylene in reaction 19.1.12 is lower than expected stoichiometrically. This indicates that additional paths of decomposition are followed during pyrolysis. The effect of  $\alpha$ - and  $\beta$ -methylation on ethyl formate on pyrolysis process has been investigated theoretically [14].

Thermal decomposition of other formic acid esters with  $\beta$ -carbon in the alcohol moiety has been reported in the literature. Examples include *n*propyl formate [15] and isopropyl formate, with the parameters in Arrhenius equation describing the decomposition  $A = 3.8 \times 10^{12} \text{ (s}^{-1}\text{)}$  and  $E^\ddagger = 44000 \pm 100 \text{ (cal)}$  [13]. The graph showing the decomposition in mole percent of isopropyl formate as a function of temperature for 1 s at the specified temperature is given in Figure 19.1.2.

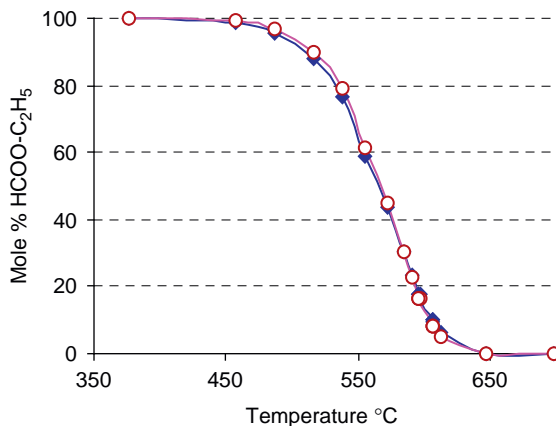


FIGURE 19.1.1. Decomposition of ethyl formate as a function of temperature, 1 s exposure.

Pyrolysis of acetic acid esters with short-chain aliphatic alcohols containing hydrogen atoms at the  $\beta$ -carbon leads, as expected, to the formation of an alkene and acetic acid [16,17]. The decomposition of ethyl acetate has the parameters in Arrhenius equation describing the decomposition  $A = 3.06 \times 10^{12}$  ( $\text{s}^{-1}$ ) and  $E^\ddagger = 47500 \pm 100$  (cal) [13] and in another estimation  $A = 3.98 \times 10^{12}$  ( $\text{s}^{-1}$ ) and  $E^\ddagger = 48000$  (cal) [18]. For isopropyl acetate the parameters in Arrhenius equation describing the decomposition are  $A = 1.0 \times 10^{12}$  ( $\text{s}^{-1}$ ) and  $E^\ddagger = 45000 \pm 100$  (cal) [13]. The graphs showing the decomposition of ethyl acetate and isopropyl acetate as a function of temperature with 1 s exposure time are given in Figure 19.1.3.

Pyrolysis of other simple esters of aliphatic acids with a larger number of carbon atoms in the acid, in the alcohol, or in both was reported in the literature [2]. Examples include cetyl palmitate (which generates palmitic acid and hexadecane), octadecyl palmitate (which generates palmitic acid and octadecene), and ethyl stearate (which generates stearic acid and ethylene). Since the organic acids and the alcohols with long hydrocarbon chains are relatively sensitive to higher temperatures, the pyrolysis reactions for their esters may take place with secondary reactions and formation of char. Therefore, when performed for synthetic purposes, the decomposition reactions must be performed at

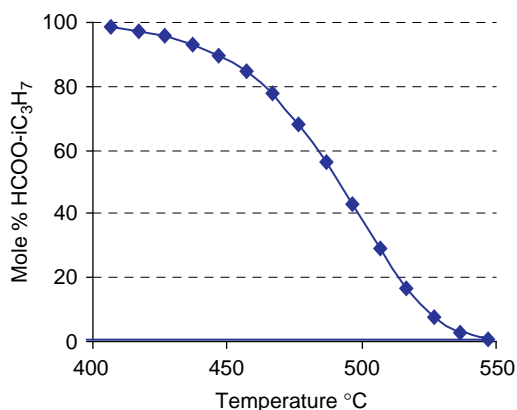


FIGURE 19.1.2. Decomposition of isopropyl formate as a function of temperature at 1 s exposure time.

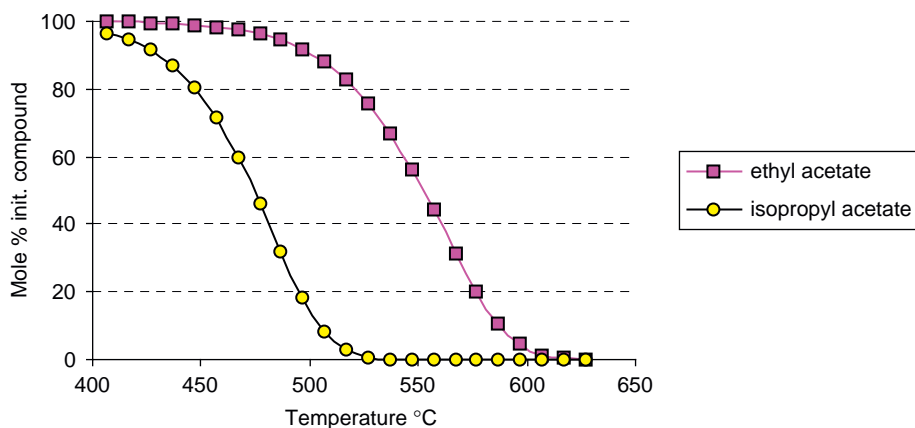
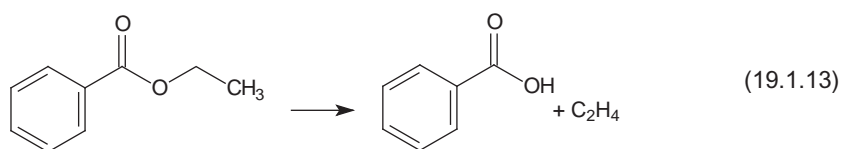


FIGURE 19.1.3. Decomposition of ethyl acetate and isopropyl acetate as a function of temperature with 1 s exposure time.

reduced pressure and at temperatures as low as possible. In this way, the yields of acid and alkene formation are in general very good.

2-Phenylethyl 2-phenylacetate decomposes following reaction 19.1.1 and generates by pyrolysis phenylacetic acid and styrene (11 h at 320 °C). Also, by the same reaction, ethyl crotonate generates ethylene and crotonic acid.

Pyrolysis of ethyl benzoate around 360 °C generates, as expected, benzoic acid and ethylene by the following reaction:



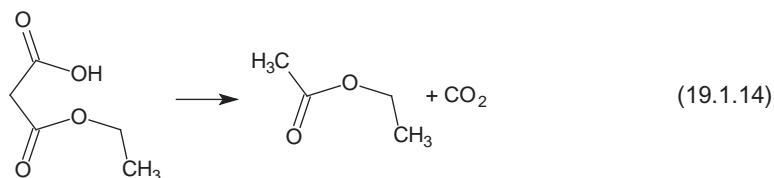
Different substituents at the benzene ring, such as 2,6-dimethyl, 2-, 3-, and 4-methoxy, 2-, 3-, and 4-amino, 2-, 3-, and 4-methyl, 2-, 3-, and 4-hydroxy, 2-, 3-, and 4-chloro, 2-, 3-, and 4-iodo, and 2-, 3-, and 4-nitro do not affect the outcome of the reaction, and the corresponding substituted benzoic acid plus ethylene are generated by pyrolysis. Kinetic results were reported for these reactions for 515 °C [19]. Pentyl benzoate generates 1-pentene and benzoic acid by pyrolysis similar to that of ethyl benzoate.

Since besides the generation of alkenes, the esters with alcohols with  $\beta$ -hydrogens generate the free acid; reaction 19.1.1 has been used to prepare some organic acids. At temperatures between 500 °C and 560 °C, the following acids were obtained from their ethyl esters with yields between 86% and 94%: hexanoic (caproic), octanoic (caprylic), dodecanoic (lauric), tetradecanoic (myristic), hexadecanoic (palmitic), octadecanoic (stearic), pentadienoic (glutaric), and 2,4,6-trimethylbenzoic [9].

### Esters of alcohols containing $\beta$ -hydrogen with dicarboxylic acids

Dicarboxylic acids can form monoesters or diesters. The diesters can be formed with the same alcohol or with different alcohols. These multiple possibilities to form esters leads to a variety of possible pyrolytic paths.

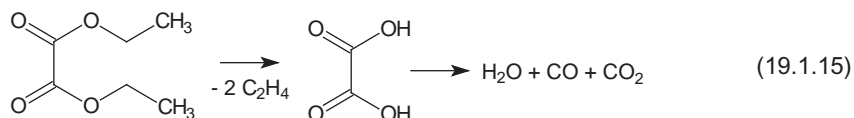
The decomposition of monoesters of dicarboxylic acids can follow two main paths. One of these is decarboxylation and the formation of a monocarboxylic acid ester. This monocarboxylic ester may further decompose as previously discussed following reaction 19.1.1. For example, oxalic acid monoethyl ester decomposes around 140 °C mainly into ethyl formate and  $\text{CO}_2$  [2]. Monoethyl malonate around 150 °C forms  $\text{CO}_2$  and ethyl acetate as the main products, and also other decomposition products such as acetic acid. The main reaction is shown below:



Another potential path is a disproportionation. For example, monoethyl succinate partially decomposes around 172 °C (in vacuum), generating diethyl succinate and succinic acid. Similar disproportionation is seen for other monoesters such as monoethyl sebacate.

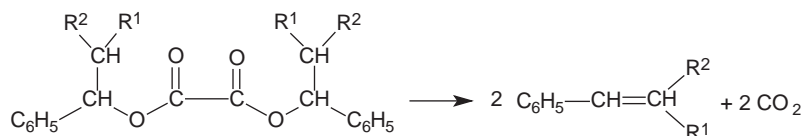
In special cases of monoester decomposition, the formation of cycles is noticed. For example, monoethyl ester of 3,6-dichlorophthalic acid forms 3,6-dichlorophthalic anhydride, the formation of phthalic anhydride being typical for several other phthalic monoesters.

Diethyl oxalate at 250 °C generates mainly CO, CO<sub>2</sub>, H<sub>2</sub>O, and C<sub>2</sub>H<sub>4</sub>. It is likely that the main reaction undergoes the model reaction 19.1.1, followed by the decomposition of the oxalic acid into CO, CO<sub>2</sub>, and H<sub>2</sub>O.

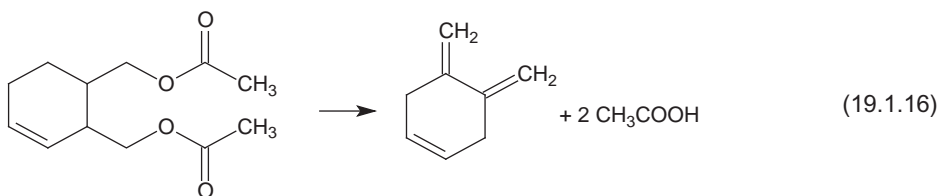


Pyrolysis of several other oxalates is reported in the literature. These include diallyl [20,21], dicrotyl, dicinnamyl, and related oxalates [20]. The main pyrolysis products from allyl and crotyl esters are condensation products of allyl radicals or crotyl radicals, respectively. The decomposition reaction was found to be a convenient source for generating these free radicals. Di-*trans*-cinnamyl oxalate generates by pyrolysis mainly indene resulting from an intramolecular cyclization.

Another group of oxalate esters studied regarding their pyrolysis results are di( $\alpha$ -substituted benzyl) oxalates [22]. When hydrogen is available in the  $\beta$ -position of the substituent, pyrolysis takes place following reaction 19.1.1, as shown below:

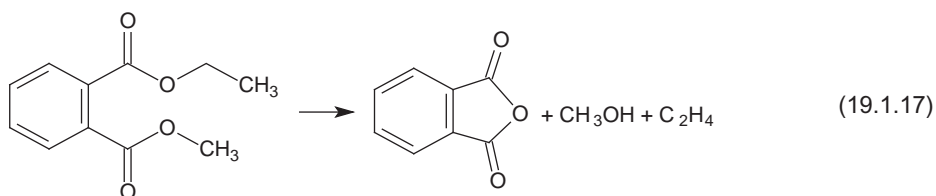


Other diesters decomposition depends considerably on the particular structure of each molecule. When  $\beta$ -hydrogens are available in the alcohol molecule, the reaction may take place independently at the two ester groups. The reaction may not require high temperatures that will affect the whole molecule, such that other moieties have the chance to remain unchanged. For example, ethyl malonate forms ethylene and malonic acid, although malonic acid further decomposes easily into  $\text{CH}_4$  and  $\text{CO}_2$ . Another example is the formation of 1,2-dimethylene-4-cyclohexene by the following reaction:

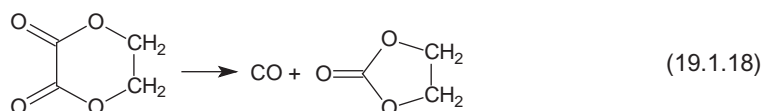


Other attempts to synthesize 1,2-dimethylene-4-cyclohexene involving eliminations (e.g., decomposition of quaternary ammonium hydroxides) led to the formation of *o*-xylene (isomer to 1,2-dimethylene-4-cyclohexene).

Different reactions may occur for other esters. For example, dibenzoyl maleic acid ester isomerizes into dibenzoyl fumarate, which decomposes with elimination of  $\text{CO}_2$  into stilbene. *o*-Phthalic esters typically generate phthalic anhydride (which is very stable to heating), an alcohol, and an alkene, as shown in the following reaction for methyl ethyl phthalate:



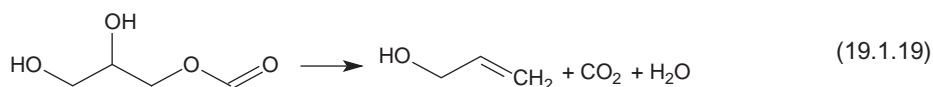
Diesters can be formed with diols, like ethyleneglycol or glycerin (in which one OH group remains free). Ethylene oxalate at 241 °C decomposes by two different paths. About 40% of the compound generates CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, and about 28% generates CO and ethylene carbonate in a reaction as shown below:



Ethylene malonate generates by pyrolysis CO<sub>2</sub>, ethyl acetate, and glycol diacetate. Ethylene succinate generates C<sub>2</sub>H<sub>4</sub> and CO<sub>2</sub>, and following a different path of decomposition, acetaldehyde and also succinic anhydride.

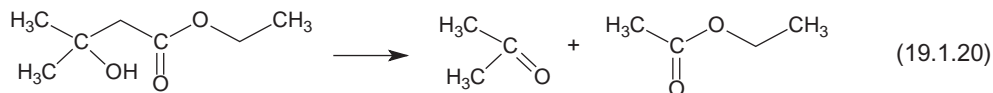
### Esters containing $\beta$ -hydrogen and additional functional groups

In many thermal decomposition reactions of esters with  $\beta$ -hydrogen in the alcohol moiety and with additional functional groups, the process still follows reaction model 19.1.1. For this reason this type of thermal decomposition was applied for the synthesis of compounds containing double bonds that are difficult to synthesize by other procedures. For example, allyl alcohol can be synthesized starting with glyceryl formate, which heated at 195 °C reacts as shown below:



The procedure can be applied in general for the transformation of a 1,2-diol into an alkene [2]. It was determined that compounds with one free alcohol group and one esterified group decompose more easily than the diesters. Formiates of 1,3-diols decompose less uniformly.

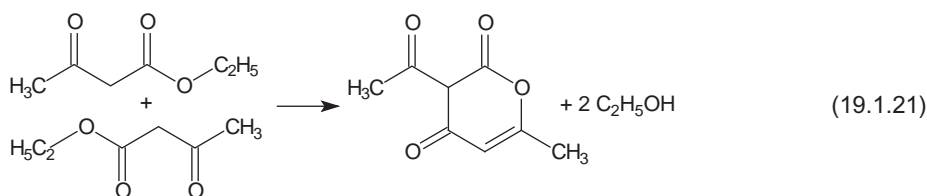
Not all cases when the alcohol moiety of the ester contains a  $\beta$ -hydrogen lead to an alkene and the acid. As an example, ethyl 3-hydroxy-3-methylbutanoate pyrolyzed in the temperature range 286–330 °C generates very little ethylene, the reaction taking place mainly with the formation of acetone and ethyl acetate by the following reaction:



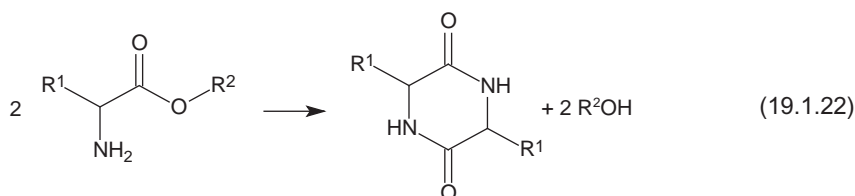
Other low-level pyrolysis products of ethyl 3-hydroxy-3-methylbutanoate include ethyl 3-methylbutenoate, acetic acid, and H<sub>2</sub>O [23]. The kinetic parameters in Arrhenius equation for the reaction 19.1.20 are  $A = 10^{12.39 \pm 0.46} \text{ s}^{-1}$  and  $E^\ddagger = 174.5 \pm 5.2 \text{ kJ/mol}$ .

Pyrolysis of esters of keto acids with the ketone groups in  $\alpha$ -position typically produces CO and the ester without the ketone functionality.  $\beta$ -Keto esters do not easily eliminate CO or CO<sub>2</sub> from their molecule. This was evaluated, for example, for the ethyl esters of acids such as glyoxylic acid (oxoacetic acid) [24,25], 2-oxopropanoic acid, and 3-methyl-2-oxobutanoic acid [25]. Their reaction typically generates a mixture of compounds, but the formation of the free acid and ethylene is an important path. For oxoacetic acid the pyrolysate also contains CO, CO<sub>2</sub>, and C<sub>2</sub>H<sub>6</sub>.

Other keto esters have different decomposition paths. For example, ethyl acetoacetate decomposition leads to ethanol and 3-acetyl-6-methyl-3-hydropyran-2,4-dione as shown below:

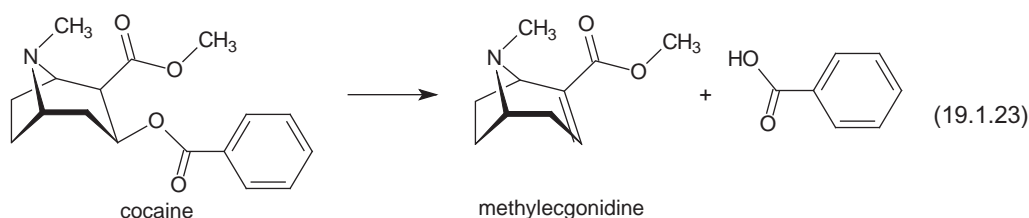


The formation of a stable six-atom cycle favors reaction 19.1.21. Six-atom heterocycles are also generated from the pyrolysis of the esters of  $\alpha$ -amino acids. Similar to the free amino acids, but typically with higher yields, the esters of  $\alpha$ -amino acids generate diketopiperazines (see Chapter 18). The general reaction is the following:

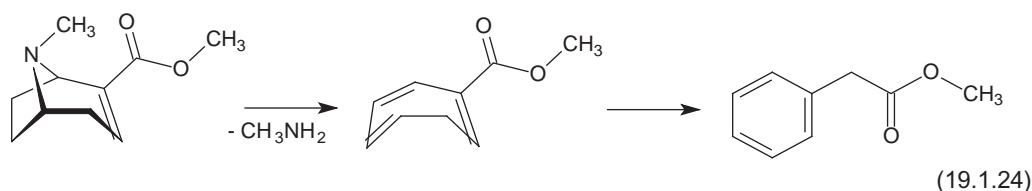


$\beta$ -Amino esters decompose in a more complicated manner, typically generating by pyrolysis a complex mixture of molecules.

In the group of esters containing additional functionalities many complex molecules can be included. One example is cocaine. This molecule has a  $\beta$ -hydrogen in the alcohol and decomposes by reaction 19.1.1. At 650 °C cocaine forms methylecgonidine (anhydroecgonine methyl ester) and benzoic acid with yields between 83% and 89% of the initial compound [26,27]. The reaction is shown as follows:



Methylecgonidine can be used for the detection of cocaine for forensic purposes. Other degradation products of cocaine include traces of cocaethylene and norcocaine (see Section 6.4). Also, compounds resulting from the rearrangement of methylecgonidine were detected in the pyrolysate including methyl phenylacetate, *o*-, *m*-, and *p*-toluates, etc. [28]. The formation of methyl phenylacetate is shown in the following reaction:



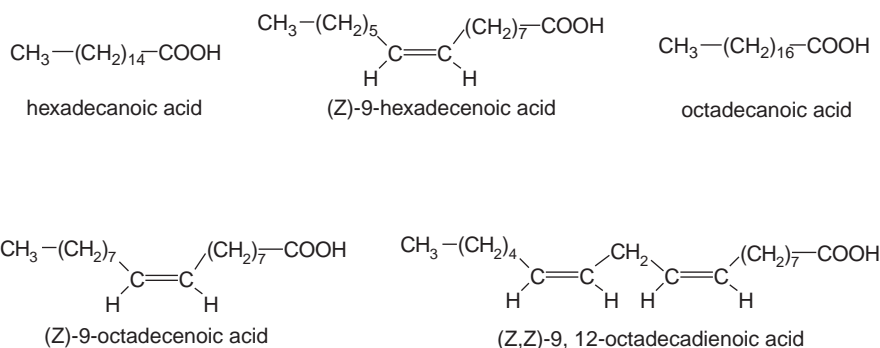
Similar rearrangements of the 1,3,5-cycloheptatriene cycle lead to the other pyrolysis products.

## Lipids

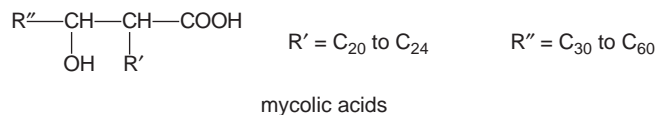
Lipids are bioorganic substances related to the esters of long hydrocarbon chain carboxylic acid (fatty acids). The class includes a variety of compounds, which is explained by the fact that initially the term *lipids* was used to describe natural bioorganic substances soluble in nonpolar solvents and insoluble in water. Lipids include both small molecules and polymeric materials. Pyrolysis of polymeric lipids is beyond the scope of this book, and information on this subject is reported in the literature (see, e.g., [29]). In nature, non-polymeric lipids are commonly mixed with polymeric ones, and pyrolytic techniques frequently have been applied on the whole lipid material without separation. This was done, for example, in the case of classification and identification of microorganisms based on analytical pyrolysis results used to identify their fatty acid content [30].

A number of classifications of lipids have been proposed. One such classification distinguishes simple lipids, phosphoglycerides, sphingolipids, glycolipids, peptidolipids, and peptidoglycolipids, the last three classes consisting mostly of polymeric compounds.

Simple lipids include several groups of compounds such as glycerol esters, cholesterol esters, and waxes. Glycerol esters represent the largest group of simple lipids, and these compounds are very common in plants and animals. The esters can be mono-, di-, or triglycerides, since glycerol has three OH- esterifying groups. The acids that esterify glycerol are fatty acids. There are significant differences in the distribution of acids in fats between land animals, aquatic animals, microorganisms, plants, etc., and even between different species [31]. The acids comprise both saturated and unsaturated acids, commonly with C<sub>14</sub>–C<sub>20</sub> carbon atoms. Among the most common acids are (Z)-9-octadecenoic acid (oleic acid), hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), (Z)-9-hexadecenoic acid (palmitoleic acid), and (Z,Z)-9,12-octadecadienoic acid (linoleic acid). These acids are shown below:



Acids containing a wider range of carbon atoms between C<sub>4</sub> and C<sub>34</sub> or higher are also found as glycerides. Besides simple acids, more complex ones such as branched and/or hydroxylated acids are also common mainly in the lipids from microorganisms. One group of such acids is, for example, the mycolic acids:

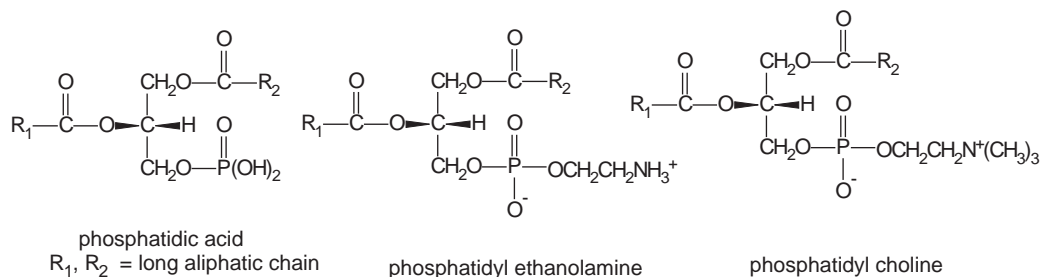


Among the simple lipids are the cholesterol esters formed with acids such as palmitic, stearic, or oleic. These compounds are common compounds in most animal cells, although not in plants. Besides cholesterol, other zoosterols are also known [31]. Several sterols and their esters are present in plants (phytosterols), the most common being the esters of sitosterol(s) and stigmasterol (see Section 9.1).

The waxes include a variety of esters of long-chain aliphatic acids with long-chain aliphatic alcohols. As an example, beeswax is an impure mixture of esters of acids CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>COOH where  $n = 24$  to  $34$

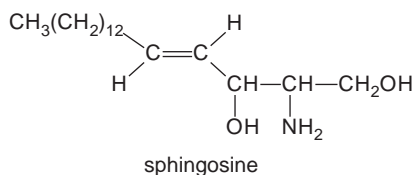
with alcohols  $\text{CH}_3(\text{CH}_2)_m\text{CH}_2\text{OH}$  where  $m = 24, 26, 28, 30, 32,$  and  $34$ . The impurities consist of free acids, fats, hydrocarbons, esters of hydroxy acids, etc.

Phosphoglycerides are fats in which the three OHs of glycerol are esterified with two fatty acids and one phosphoric acid. Glycerol esters of phosphoric acid containing a free OH— glycerol group and only one fatty acid, as well as compounds with an ether linkage at one OH— glycerol group named plasmalogens, are also present in nature. The phosphoric acid moiety can be further esterified (phosphoric acid is a tribasic acid). This esterification can be done with ethanolamine (in cephalins), choline (in lecithins), serine, inositol, etc. Some of these compounds are shown below:



Phosphoglycerides with the phosphoric acid moiety further esterified with inositol may generate more complex compounds, since inositol can be connected with glycosyl residues.

Sphingolipids form a lipid class that does not contain glycerol. In this class, sphingomyelins, cerebrosides, gangliosides, and sulfatides are included. The compounds from this class can be considered as derived from sphingosine or related substances such as dehydrosphingosine (sphinganine), 4-hydroxy-sphinganine, etc. For example, sphingomyelins are sphingosine phosphatides where the amino group in sphingosine is acylated with a fatty acid radical such as stearyl, palmityl, etc., and the primary alcohol group forms a phosphatide (primary alcohol is esterified with a phosphoric unit itself esterified with choline at the second site).



Cerebrosides (glycosylceramides) are formed from sphingosine where the amino group is acylated with a fatty acid radical (as in sphingomyelins), but the primary alcohol group forms an ether bond with a sugar (polysaccharide) residue. Di-, tri-, and tetraglycosylceramides are found in mammalian tissues, mainly in the central nervous system. When the glycosylceramides contain residues of *N*-acetylneuraminic acid, the substances are considered to form a separate class known as gangliosides. The length of the sugar chain may vary, and gangliosides with more than one acetylneuraminic acid residue are known. These compounds can be considered organic polymers (see, e.g., [29]).

Glycolipids can be simple glycosyl diacylglycerols, such as mono- $\text{D}$ -galactopyranosyl diacylglycerols, where the common acyl groups are stearyl, oleyl, linoleyl, etc. More complex glycolipids are also found in biological samples. Most of them are analogous with other lipids described previously but having a sugar moiety attached through ester or ether bonds and forming polymeric compounds. Other glycolipids are carbohydrate esters of fatty acids (such as mycolic acids). Mycosides are part of this group, and they contain a branched aliphatic chain with hydroxyl groups esterified by fatty acids and terminated at one end by a phenol group to which the carbohydrate moiety is linked.

Peptidolipids and peptidoglycolipids are present in bioorganic materials and are mostly polymeric lipids.



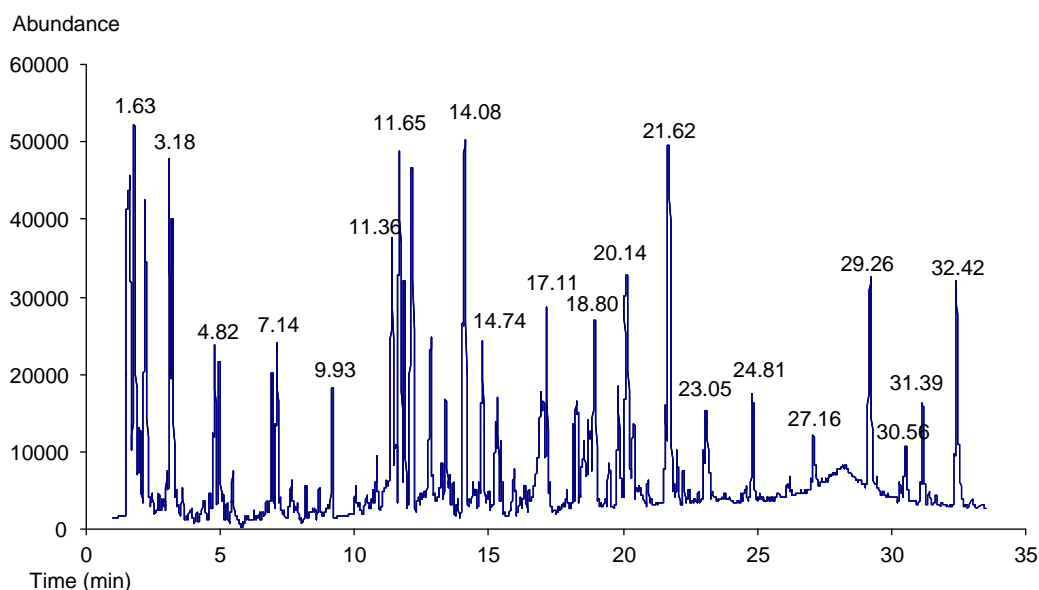
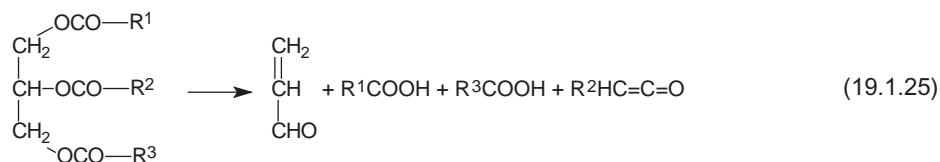


FIGURE 19.1.4. Pyrogram of olive oil at 750 °C [34]. Peak assignment given in Table 19.1.1.

Pyrolysis of lipids has been studied with the purpose of understanding their behavior when heated [32–41] and also for analytical purposes [42–64]. Thermal decomposition of triglycerides starts at temperatures above 200 °C and generates mostly hydrocarbons, carboxylic acids, a few carbonyl compounds, and possibly some alcohols [34]. Pyrolysis of olive oil, which contains a very high proportion of triolein, performed at a  $T_{\text{eq}} = 750$  °C for 15 s and analyzed by GC/MS generated the pyrogram as shown in Figure 19.1.4 [34]. The separation of pyrolysate was done on a 30 m HP5-MS column, which was held at an initial temperature of 40 °C for 2 min, then ramped at 8 °C/min to a final temperature of 300 °C where it was held for 5 min. The peak identification (some tentative) done with mass spectral library searches is given in Table 19.1.1.

Most decomposition products of olive oil are hydrocarbons, carboxylic acids shorter than oleic acid, and some aldehydes. The main pyrolysis paths in triglyceride pyrolysis start with the ester decomposition, following basically the following reaction:



This initial reaction is followed by many further decomposition processes including the following [40]:

- Decomposition of fatty acids by reactions described in Chapter 17, including  $\text{R}-\text{COOH} \rightarrow \text{RH} + \text{CO}_2$ ,  $2\text{R}-\text{COOH} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{RHC}=\text{CHR}$ , etc.
- Decomposition of acrolein:  $\text{CH}_2=\text{CHCHO} \rightarrow \text{CO} + \text{C}_2\text{H}_4$ , etc.
- Decomposition of ketenes:  $2\text{R}^2\text{HC}=\text{C}=\text{O} \rightarrow 2\text{CO} + \text{R}^2\text{HC}=\text{CHR}^2$  and other reactions.
- Decomposition in elements to generate char and possibly  $\text{H}_2$ .
- Further decomposition of alkanes  $\text{RH}$  and alkenes  $\text{RHC}=\text{CHR}$  to form various alkenes and alkadienes as described in Chapter 7.
- Formation of aromatic hydrocarbons from alkanes and alkenes decomposition.
- Some reduction reactions as a result of  $\text{H}_2$  generated in some decompositions.

TABLE 19.1.1. Peak identification in the pyrogram shown in Figure 19.1.4 for the pyrolysis of olive oil (mostly triolein) at 750°C (hydrogen, methane, and ethylene were not analyzed due to the mass spectrometer settings)

No.	Ret. time (min)	Compound
1	1.52	Carbon dioxide
2	1.63	Propene
3	1.84	2-Propenal
4	1.97	Ethylidenecyclopropane
5	2.02	2-Methyl-1-buten-3-yne
6	2.09	Cyclopentene
7	2.26	1-Hexene
8	2.30	Hexane
9	2.42	(Z,Z)-1,4-Hexadiene
10	2.54	Cyclohexane
11	2.77	1,3-Hexadiene
12	2.87	Benzene
13	2.97	1,3-Cyclohexadiene
14	3.08	Ethenylcyclobutane
15	3.18	1-Heptene
16	3.29	Heptane
17	3.39	2-Heptene
18	4.66	Cyclooctene (Z?)
19	4.82	1-Octene
20	4.99	Octane
21	5.12	(Z)-2-Octene
22	5.52	Cyclooctene (E?)
23	6.95	1-Nonene
24	7.14	C <sub>8</sub> H <sub>16</sub>
25	8.23	1-Butyl-cyclopentene
26	9.18	1-Decene
27	9.37	C <sub>10</sub> H <sub>20</sub>
28	9.50	(E)-2-Decene
29	9.93	1,3-Octadiene
30	11.36	C <sub>9</sub> H <sub>18</sub>
31	11.65	5-Undecene
32	11.84	(E)-2-Undecene
33	12.08	(E,E)-1,3-Nonadiene
34	12.79	Undeca-2Z,4E-diene
35	12.91	(E)-Bicyclo[5.1.0]octane
36	13.17	Octanoic acid
37	13.38	1-Dodecene
38	13.48	(Z)-3-Dodecene
39	13.55	Dodecane
40	13.65	(E)-4-Dodecene
41	14.08	5-Decyne
42	14.74	(E,Z)-2,4-Dodecadiene
43	15.21	(Z)-Cyclodecene

(Continued)

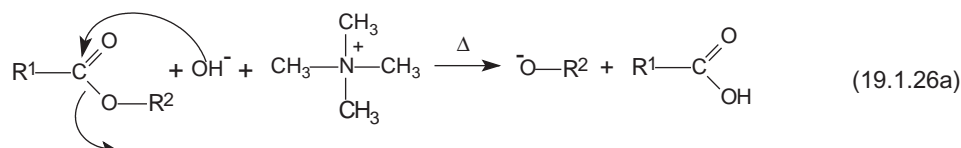
TABLE 19.1.1. *cont'd*

No.	Ret. time (min)	Compound
44	15.30	1-Tridecene
45	15.45	Tridecane
46	16.32	Cyclotridecane
47	16.99	<i>n</i> -Decanoic acid
48	17.11	1-Tetradecene
49	17.23	Tetradecane
50	17.79	1,9-Tetradecadiene
51	18.13	Cyclotetradecane
52	18.47	1-Octylcyclohexene
53	18.54	( <i>Z,Z</i> )-1,6-Tridecadiene
54	18.58	( <i>Z</i> )-9-Tetradecen-1-ol
55	18.67	Cyclododecane
56	18.72	Cyclopentadecane
57	18.80	( <i>E</i> )-2-Tetradecene
58	18.93	Pentadecane
59	19.83	<i>n</i> -Nonylcyclohexane
60	19.89	7-Hexadecyne
61	20.14	( <i>E</i> )-Cyclododecene
62	20.19	1-Hexadecyne
63	20.29	Cyclohexadecane
64	20.40	1-Hexadecene
65	20.51	Hexadecane
66	21.62	1,13-Tetradecadiene
67	21.74	8-Heptadecene
68	22.02	Heptadecane
69	22.28	1-Methylcyclododecane
70	23.05	1-Methyl-2-methylenecyclohexane
71	23.14	( <i>E</i> ?) -5-Octadecene
72	23.22	( <i>Z</i> ?) -5-Octadecene
73	24.81	( <i>Z</i> )-9-Octadecenal
74	24.87	( <i>Z,Z</i> )-9,12-Octadecadienoic acid
75	26.87	( <i>Z,Z</i> )-9,17-Octadecadienal
76	27.16	Unknown
77	27.23	(?,?) -Octadecadienoic acid
78	27.40	( <i>Z,E</i> )-2,13-Octadecadien-1-ol
79	27.68	Hexadecenoic acid?
80	27.78	2-Methyl-3 <i>Z</i> ,13 <i>Z</i> -octadecadienol
81	27.84	(?,?) -Octadecadienol
82	27.98	2-Octylcyclopropaneoctanol
83	28.04	2-Methyl-?,?-octadecadienol
84	28.11	( <i>Z,E</i> )-3,13-Octadecadien-1-ol
85	28.14	11-Hexadecen-1-ol acetate
86	28.19	9-Octadecenoic acid
87	28.26	Hexadecenol ecetate?
88	28.31	1-Docosane
89	29.26	(?,?) -Octadecadien-1-ol

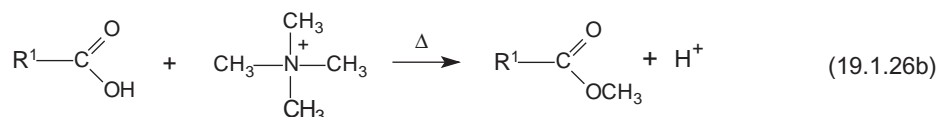
TABLE 19.1.1. *cont'd*

No.	Ret. time (min)	Compound
90	29.52	2-Methyl-?,?-octadecadienol
91	29.68	Oleic acid
92	30.56	Cyclooctatetraene
93	31.39	(Z)-9-Octadecenal
94	32.42	(Z,E)-2,13-Octadecadien-1-ol acetate

A considerable number of studies were reported regarding analytical pyrolysis of lipids, particularly of triglycerides. Successful procedures were developed using pyrolysis/derivatization with tetramethylammonium hydroxide (TMAH) and other hydrolysis/alkylating reagents for the analysis of fatty acid composition of triglycerides and waxes [42]. The procedure consists of pyrolyzing together the lipid and the reagent at temperatures around 750 °C followed by GC/MS analysis of the methyl esters generated during this process. The derivatization reactions occurring in these procedures with, for example, TMAH as a reagent starts with the hydrolysis of the lipid, as shown in the following reaction:



The free acid further reacts with the reagent as shown below:

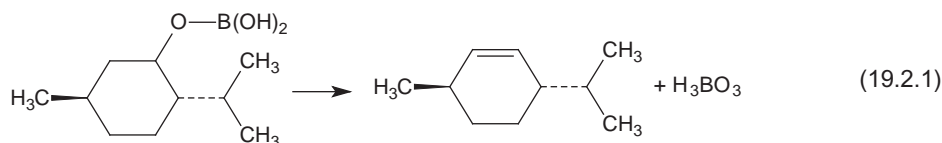


The end result consists of methyl esters of the acids and formation of free alcohols, which were participating in the lipid molecule. Most studies were done for lipid fatty acids determination on various natural lipids such as specific types of oils (peanut [45], cocoa butter [46], oils from Macauba fruit [47]), whole-cell microorganisms, with the purpose of characterization and differentiation, etc.

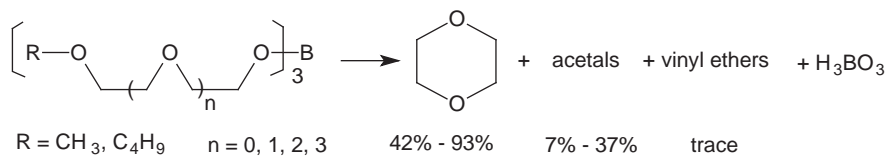
## 19.2. INORGANIC ESTERS

### General aspects

Oxygenated inorganic acids such as boric  $\text{H}_3\text{BO}_3$  or  $\text{B}(\text{OH})_3$ , carbonic  $\text{H}_2\text{CO}_3$ , nitrous  $\text{HNO}_2$ , nitric  $\text{HNO}_3$ , phosphoric  $\text{H}_3\text{PO}_4$ , and sulfuric  $\text{H}_2\text{SO}_4$  can also generate esters by replacing an OH group with an alkoxy or phenoxy group  $-\text{OR}$ . Boric esters are formed easily by the heating of boric anhydride with an alcohol. The decomposition of borates (orthoborates) of alcohols with  $\beta$ -hydrogens takes place following reaction 19.1.1 with the formation of an alkene and boric acid, as shown for a borate of menthol below [65]:

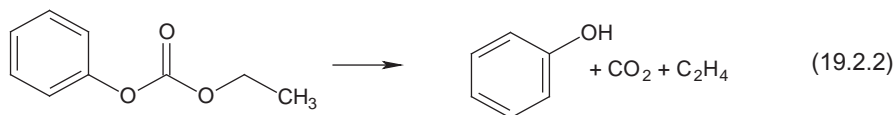


Pyrolysis of alkoxy ethyl borates generates mainly dioxane, acetals, and traces of vinyl ethers [66]. The reactions are shown below:



The decomposition of other borate esters is reported in the literature, such as benzyl borate [67] and borates derived from catechol, which are used as flame retardants [68].

The monoesters of carbonic acid are not stable. The diesters typically decompose with elimination of  $\text{CO}_2$  and other molecular fragments. Kinetic parameters of diethyl carbonate decomposition are given in the literature [69]. The carbonates esterified with phenols generate by decomposition  $\text{CO}_2$ , and the phenol as shown below for phenyl ethyl carbonate:

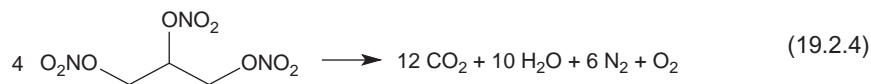


Pyrolysis of esters of nitrous acid was also studied, in particular related to the equilibrium nitrite-nitro derivative [70,71]. For example, nitromethane may be in equilibrium with methyl nitrite, as shown in the following reaction:



When a  $\beta$ -hydrogen exists in the alcohol (e.g., in ethyl nitrite), the decomposition at relatively low temperatures generates the alkene,  $\text{H}_2\text{O}$ , and  $\text{NO}$ . When no  $\beta$ -hydrogen is available, thermal decomposition takes place by a free-radical mechanism with the formation of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ , and a mixture of hydrocarbons. Kinetic studies on some nitrites pyrolysis were reported in the literature [72].

Pyrolysis of nitric acid esters is described in a number of publications, particularly due to the interest in energetic materials [73]. Some of these compounds decompose explosively. For example, glycerin trinitrate decomposes upon heating following the reaction:



The bond  $\text{O}-\text{NO}_2$  in nitrate esters is typically cleaved upon heating at relatively low temperatures between  $150^\circ\text{C}$  and  $200^\circ\text{C}$  in a reaction as shown below:



The free radicals formed in reaction 19.2.5 further undergo different reactions, depending on the nature of radical  $\text{R}$ , and generate a variety of compounds. The formation of several decomposition

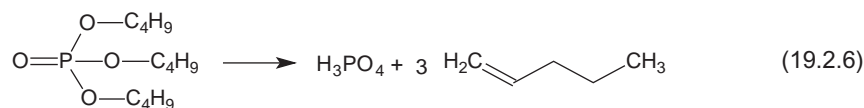
Chemical reaction scheme showing the degradation pathways of benzyl nitrate:

c1ccccc1CCO[N+](=O)[O-].[O-]N=O>>c1ccccc1CCO[N+](=O)[O-].[O-]

Pathways from the benzyl radical:

- $\text{Ph-CH}_2\text{-CH}_2\text{-O}^\bullet \xrightarrow{-\text{CH}_2=\text{O}} \text{Ph-CH}_2^\bullet \xrightarrow{+\text{H}^\bullet} \text{Ph-CH}_3$
- $\text{Ph-CH}_2\text{-CH}_2\text{-O}^\bullet \xrightarrow{+\text{NO}} \text{Ph-CH}_2\text{-CH}_2\text{-O-NO}^\bullet \xrightarrow{-\text{H}_2\text{O}} \text{Ph-CHO}$
- $\text{Ph-CH}_2\text{-CH}_2\text{-O}^\bullet \xrightarrow{+\text{O}_2} \text{Ph-CH}_2\text{-CH}_2\text{-O-O}^\bullet \xrightarrow{+\text{H}^\bullet} \text{Ph-CH}_2\text{-CH}_2\text{-OH}$
- $\text{Ph-CH}_2\text{-CH}_2\text{-O}^\bullet \xrightarrow{+\text{O}_2} \text{Ph-CO}^\bullet \xrightarrow{-\text{HO}^\bullet} \text{Ph-CHO}$

Phosphoric acid is the usual name for orthophosphoric acid  $\text{H}_3\text{PO}_4$ . However, several other acids of phosphorus in valence V are known, including pyrophosphoric acid  $\text{H}_4\text{P}_2\text{O}_7$ , tripolyphosphoric acid  $\text{H}_5\text{P}_3\text{O}_{10}$ , etc. Also phosphorus in valence III forms an oxygenated acid able to form organic phosphites  $\text{P}(\text{OR})_3$ . Phosphoric acid esters are common organic compounds with various industrial uses such as lubricants and hydraulic fluids (aryl phosphates), chelating reagents in plutonium separation plants (tributyl phosphate), etc. Certain phosphate esters are important compounds in biological systems (adenosine diphosphate, ADP; adenosine triphosphate, ATP; and glucose 6-phosphate). Phosphoric acid is able to form mono, di and tri esters. Phosphates are in general stable compounds to heating. At temperatures above  $300^\circ\text{C}$ , simple phosphates generated from alcohols with a  $\beta$ -hydrogen decompose following reaction 19.1.1 to form alkenes and the acid, shown as follows for tributyl phosphate:



As shown in Table 19.2.1, the decomposition of glucose 6-phosphate monosodium salt generates much less levoglucosan and considerably more 5-(hydroxymethyl)-2-furancarboxaldehyde (hydroxymethylfurfural). The low level of levoglucosan shows that the elimination of  $\text{NaH}_2\text{PO}_4$  between the phosphate group and the H from the OH group in 1-position of glucose is not a favored reaction.

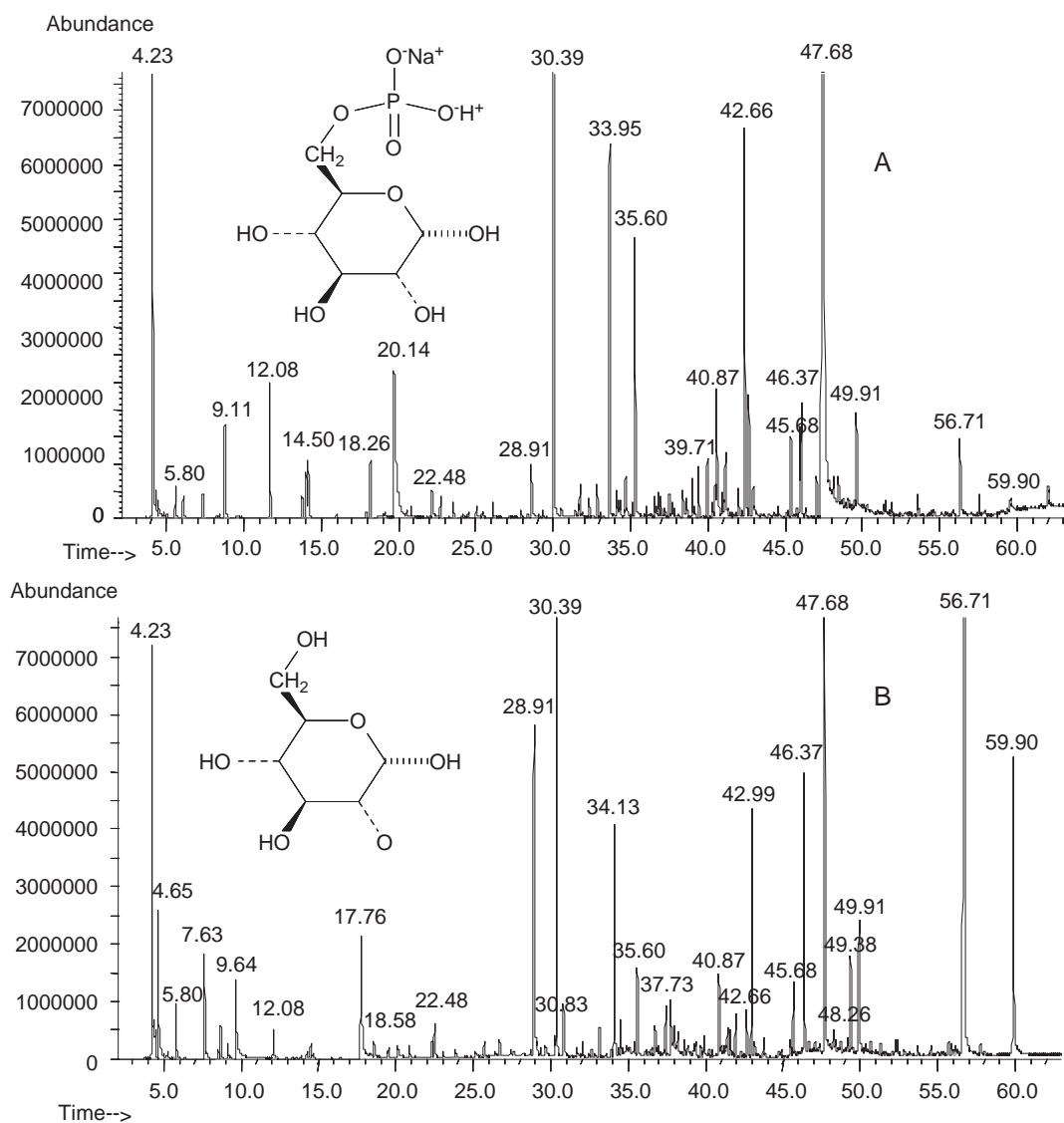


FIGURE 19.2.1. Pyrogram of 2.0 mg D-(+)-glucose 6-phosphate Na salt (trace A) and 1.0 mg glucose (trace B) at 900°C (see Figure 16.1.5).

TABLE 19.2.1. Identification of the main peaks in the pyrogram of D-(+)-glucose 6-phosphate Na salt (trace A in Figure 19.2.1) and comparison with mole percent of identical compounds from 1.0 mg glucose pyrolysate (trace B in Figure 19.2.1)

No.	Compound	Ret. time (min)	MW	CAS no.	Glucose 6-phosphate (mol%)	Glucose (mol%)
1	Carbon dioxide	4.23	44	124-38-9	<b>16.27</b>	<b>10.37</b>
2	Formaldehyde	4.65	30	50-00-0	0.46	<b>6.73</b>
3	Acetone	9.11	58	67-64-1	1.78	0.50
4	2-Methylfuran	12.08	82	534-22-5	1.67	0.57
5	2,3-Butanedione	14.50	86	431-03-8	0.79	0.21

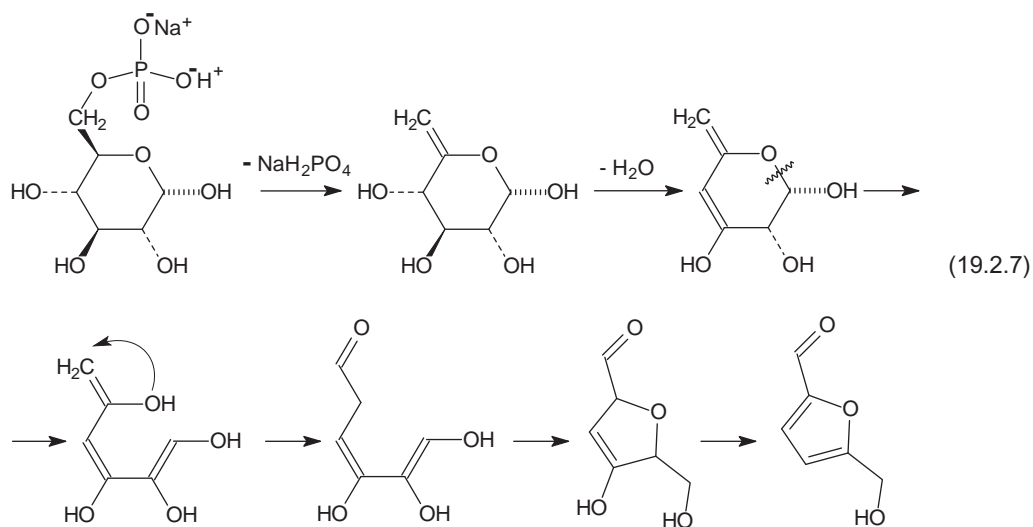
TABLE 19.2.1. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Glucose 6-phosphate (mol%)	Glucose (mol%)
6	Acetic acid	20.11	60	64-19-7	<b>5.65</b>	0.37
7	1,4-Dioxadiene	28.91	84	N/A	0.75	<b>5.79</b>
8	Furfural	30.39	96	98-01-1	<b>5.65</b>	<b>11.49</b>
9	2,4-Dihydroxy-2,5-dimethyl-2(2H)-furan-3-one	33.95	144	10230-62-3	1.97	Trace
10	5-Methyl-2-furancarboxaldehyde	35.60	110	620-02-0	1.93	1.04
11	3-Furancarboxylic acid methyl ester	40.87	126	13129-23-2	1.20	0.87
12	2,5-Furandicarboxaldehyde	41.42	124	823-82-5	0.80	0.49
13	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	42.66	144	28564-83-2	2.65	0.46
14	Levoglucosenone	42.99	126	37112-31-5	0.71	2.19
15	5-Acetoxymethyl-2-furaldehyde	45.68	168	10551-58-3	0.38	0.74
16	1,4:3,6-Dianhydro- $\alpha$ -D-glucopyranose	46.37	144	N/A	0.86	2.67
17	5-(Hydroxymethyl)-2-furancarboxaldehyde	47.68	126	67-47-0	<b>43.26</b>	<b>10.33</b>
18	Dianhydrosugar?	49.91	144	N/A	0.72	1.30
19	1,6-Anhydro- $\beta$ -D-glucopyranose (levoglucosan)	56.72	162	498-07-7	0.55	<b>11.00</b>
	Total*				88.05	67.12

Note: Numbers in bold indicate the major pyrolysis constituents.

\*Since only some major peaks were considered in Table 19.2.1, the total is not 100.

This reaction would have been similar to the elimination of water from glucose by reaction 16.1.12. A reaction similar to 19.1.1 may be the first step in the pyrolysis. This reaction is then followed by a series of water eliminations and rearrangements that lead to the formation of hydroxymethylfurfural shown as follows:

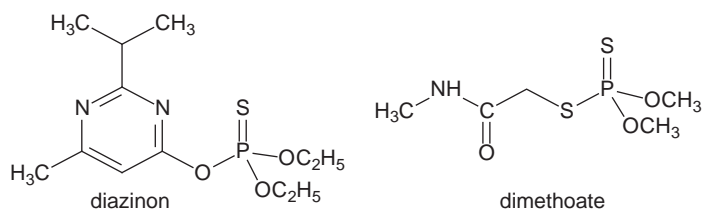




Phosphates of phenols (aryl phosphates) are stable compounds. Pyrolysis starts only around 600–700 °C, mainly with the formation of polycyclic aromatic hydrocarbons (PAHs). Two mechanisms were suggested for the formation of PAHs, one being the formation of aryl radicals that further interact to form PAHs, and the second assuming the breaking of some aromatic rings with formation of unsaturated noncyclic fragments that further interact to form PAHs [82]. Several studies were performed on pyrolysis of tricresyl phosphate, which is used as a plasticizer in polymers and additive in lubricants. The commercial product is a mixture of *o*-, *m*-, and *p*-tricresyl phosphate, and the concern is its distillation at elevated temperatures rather than the formation of pyrolysis products, since *o*-tricresyl phosphate is neurotoxic. Pyrolysis of these compounds at temperatures above 700 °C generates mainly PAHs, H<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, and char [83].

A number of phosphate esters are important biological compounds. Examples include phytic acid or inositol hexakisphosphate, which is the principal storage form of phosphorus in many plant tissues; ATP and ADP, which are nucleotides necessary for intracellular energy transfer; cyclic adenosine monophosphate (cyclic AMP); etc. Pyrolysis of these compounds is expected to generate similar compounds with those generated by the associated alcohol (e.g., adenosine for ATP, ADP, and AMP) [29].

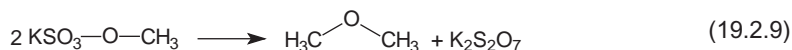
Pyrolysis of esters of thiophosphoric acids (one or more oxygen atoms in H<sub>3</sub>PO<sub>4</sub> molecule replaced with sulfur) are also reported in the literature [84]. Some of these compounds are used as efficient insecticides such as diazinon and dimethoate.



Sulfuric acid is capable of forming mono and diesters. Monoesters of short-chain aliphatic alcohols decomposes above 100 °C following reaction 19.1.1, as shown in the following reaction for monoethyl sulfate:



The decomposition of the sulfate may also be conducted to form dialkyl ether, as shown below for potassium methyl sulfate:



Diethyl ether can be generated from ethyl sulfate by a similar procedure, but sulfuric acid esters with alcohols with longer alkyl groups than two carbons tend to form mainly the alkene. The study of reaction kinetics of alkyl hydrogen sulfates is reported in the literature [85].

A number of anionic surfactants are monoesters of sulfuric acid with long alkyl chain alcohols or with alkylphenols. Pyrolysis of these surfactants at 650 or 700 °C has been used for surfactant analysis since the generated fragments can be used for the surfactant identification [86]. Paraffin sulfates give primarily  $\alpha$ -olefins, and alkyl–aryl sulfates generate aromatic hydrocarbons,  $\alpha$ -olefins, etc. Addition of an acid (such as H<sub>3</sub>PO<sub>4</sub>) [87,88] or of an alkali metal hydroxide [89] was used during analytical pyrolysis of certain surfactants, with the purpose of generating characteristic fragments. The addition of phosphoric acid allows complete desulfonation, and the fragments resulting from pyrolysis are of hydrocarbon type and easier to analyze.

Pyrolytic reactions for other inorganic esters also were described in the literature. For example, diethyl sulfite by thermal decomposition at 200 °C generates mainly diethyl ether and SO<sub>2</sub>. Hypochlorous acid esters with primary and secondary alcohols have been used to generate carbonyl

compounds by thermal decomposition [2]. Esters of acids with trimethylsilanol are commonly used after derivatization with specific reagents for analytical purposes [90]. These compounds are relatively stable to heating, as they should remain unmodified during the gas chromatographic separation at temperatures as high as 400 °C.

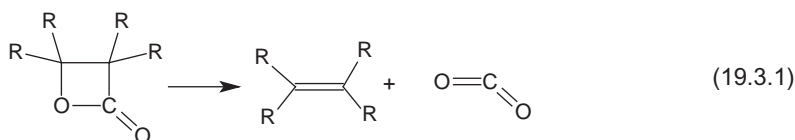
### 19.3. LACTONES

#### General aspects

Lactones are cyclic esters formed by water elimination between the COOH group and the OH group present on the same molecule. Lactones are generated easily from hydroxy acids when a five-atom ring ( $\gamma$ -lactones) or a six-atom ring ( $\delta$ -lactones) is formed. Other lactones ( $\beta$ ,  $\epsilon$ , etc.) are also known, but they are more difficult to synthesize directly from the acid, and their stability is typically lower than that of lactones with five- or six-atom rings.

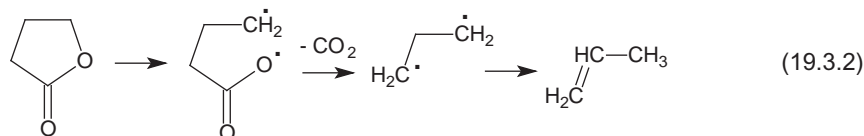
#### Simple lactones

$\beta$ -Lactones are typically decomposed with CO<sub>2</sub> elimination and formation of an unsaturated compound. This reaction is shown below in general form:



For example,  $\beta$ -butyrolactone generates CO<sub>2</sub> and propene. Similarly,  $\alpha,\alpha$ -dimethyl- $\beta$ -butyrolactone (3,3,4-trimethyloxetan-2-one) generates CO<sub>2</sub> and 2-methylbut-2-ene.

$\gamma$ -Butyrolactone is the simplest  $\gamma$ -lactone. The compound is stable to heating and decomposes above 500 °C by decarboxylation, generating CO<sub>2</sub> and propene [91]. A theoretical study on the mechanism of this reaction was reported in the literature [92]. The reaction probably takes place by a series of consecutive steps shown as follows:

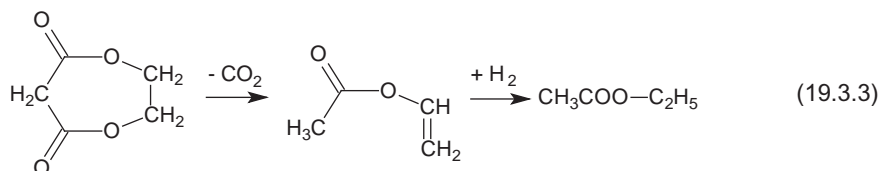


A concerted mechanism was also found possible for  $\gamma$ -butyrolactone degradation since this mechanism is not significantly different regarding the activation energy as compared with the consecutive path.

Tetrahydro-2H-pyran-2-one ( $\delta$ -valerolactone) is a compound stable to heating up to about 450 °C. Its decomposition takes place with CO<sub>2</sub> elimination, but also with the formation of a number of fragment molecules.

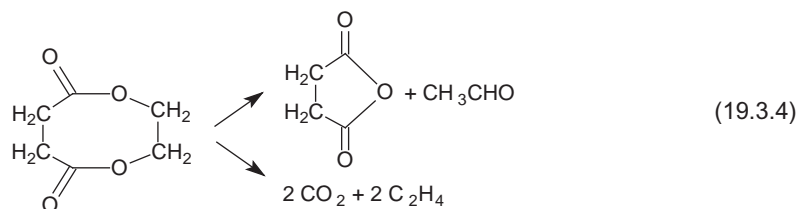
Dicarboxylic acids can form esters with dihydroxy alcohols generating cyclic esters. These esters can be considered lactones. One example is the ester of malonic acid with ethyleneglycol. The compound decomposes with the formation of CO<sub>2</sub>, acetaldehyde, ethyl acetate, ethyleneglycol diacetate, and a large proportion of char. Both reactions of formation of ethyl acetate and ethyleneglycol diacetate involve more complex transformations. The formation of ethyl acetate with addition of external

hydrogen is shown below:



Vinyl acetate was not isolated in the pyrolysate of ethyleneglycol ester of malonic acid [2].

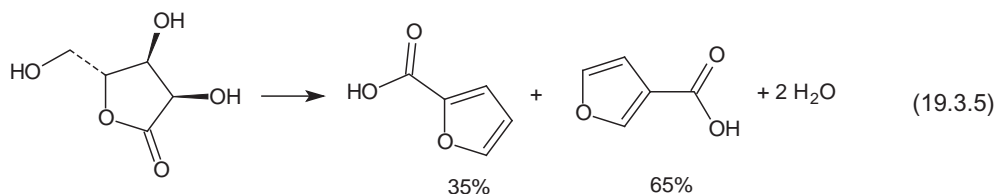
Pyrolysis of ethyleneglycol succinate takes place around 350 °C and generates acetaldehyde, succinic acid anhydride, CO<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub>. The reactions involved in this process are shown below [2]:



### Lactones containing additional functional groups

The presence of additional functional groups in a lactone molecule may influence the outcome of pyrolysis. The cleavage of the lactone group may or may not take place during pyrolysis, and the other group(s) may be involved in the decomposition reactions before the lactone group is affected. This was shown, for example, during the decomposition of some lactonic acids, which were discussed in Section 17.4. It was shown that in some cases pyrolysis takes place with decarboxylation without affecting the lactone (reaction 17.4.18). In some other cases, decarboxylation and opening of the lactone ring take place simultaneously (see reaction 17.4.19).

When groups that can be eliminated are attached to the cycle of a lactone, it is common that the cycle is transformed into a more stable aromatic heterocyclic compound. As an example, ribonic acid  $\gamma$ -lactone generates by pyrolysis a mixture of 2-furoic acid and 3-furoic acid, as shown in the following reaction:

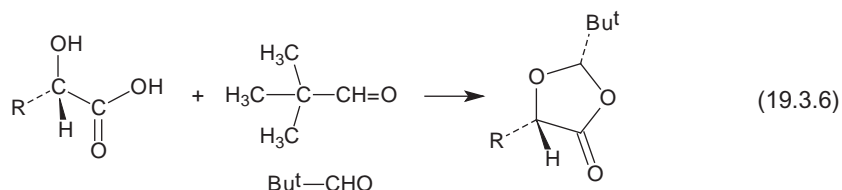


In this reaction it is likely that the lactone cycle is opened followed by a cyclization with the formation of stable furan rings.

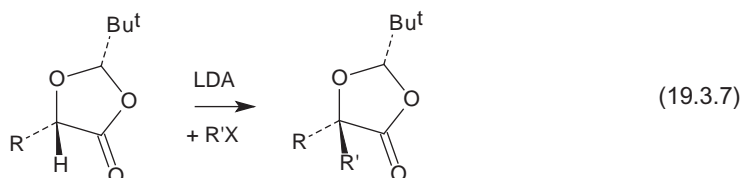
A number of natural products are related to  $\alpha$ -pyrone, including coumarine, umbeliferone, ellagic acid, etc.  $\alpha$ -Pyrone and related compounds (such as benzo- $\alpha$ -pyrone) can be considered lactones, but the special delocalization of its electronic system provides special properties to this compound, and they are viewed as heterocycles (see Section 21.1).

**1,3-Dioxolan-4-ones and 1,3-dioxan-4,6-diones**

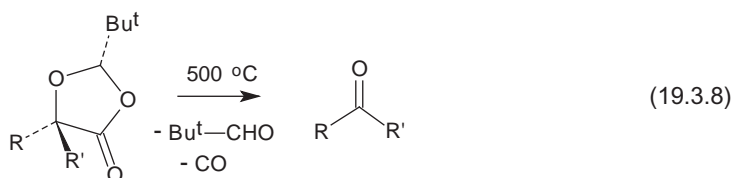
$\alpha$ -Hydroxy acids can react with aldehydes and ketones to form 1,3-dioxolan-4-ones by the following reaction, exemplified for *tert*-butyl aldehyde (pivalaldehyde):



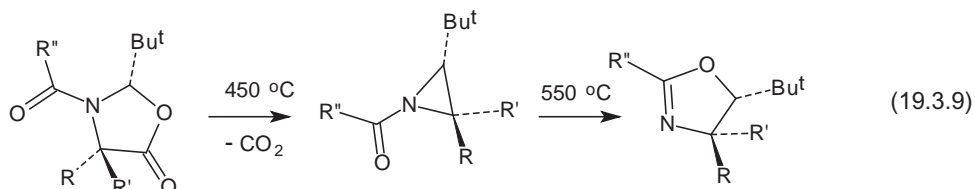
The hydrogen atom in 5-position in 1,3-dioxolan-4-one has an acidic character and can be replaced with the second radical  $\text{R}'$  in the presence of lithium diisopropylamide,  $\text{Li}^+ \text{N}^-(\text{C}_3\text{H}_7)_2$  or LDA. The reaction takes place as shown in the following reaction:



The resulting 1,3-dioxolan-4-ones can be considered lactones having an ether group in their molecule. Pyrolysis of 1,3-dioxolan-4-ones typically takes place with elimination of  $\text{CO}$ , and the initial aldehyde or ketone that reacted with the hydroxy acid, plus the formation of a new ketone, as shown in the following reaction [93]:

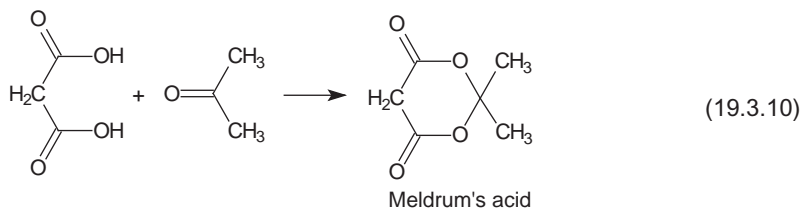


Similar to 1,3-dioxolan-4-ones, *N*-acyl-oxazolidin-5-ones can be synthesized. These compounds can be considered lactones having an amide group in their molecule. Their pyrolysis takes place differently, as shown in the following reaction:

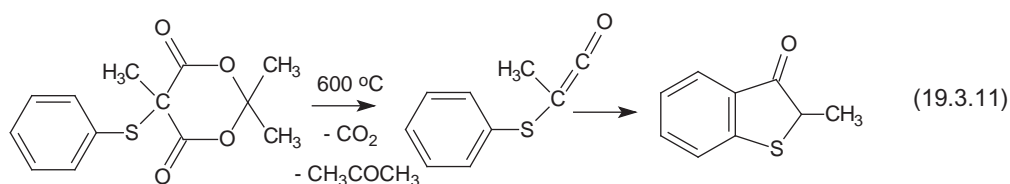


The stereochemistry of the process depends on the attached substituents  $\text{R}$ ,  $\text{R}'$ , and  $\text{R}''$  [94]. *N*-thioacyl-oxazolidin-5-ones react similarly at temperatures around  $500^\circ\text{C}$  to generate thiazolines, but without the possibility to isolate the aziridine intermediate.

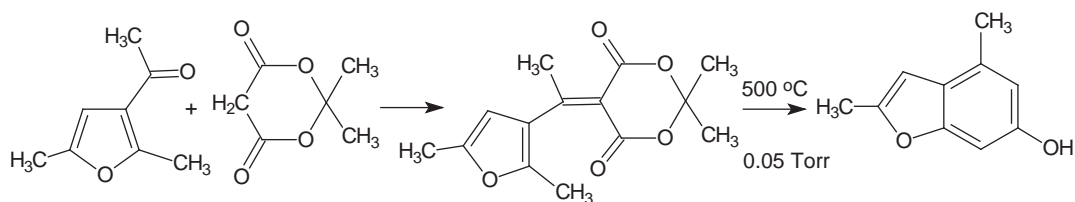
Another lactone type compound is Meldrum's acid. This compound can be synthesized from malonic acid and acetone (in acetic anhydride and a strong Lewis acid). The reaction is shown below:



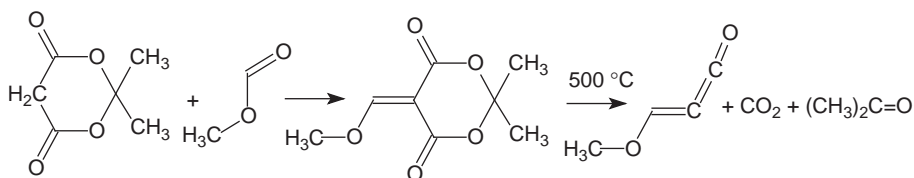
The hydrogens at the  $\text{CH}_2$  group in Meldrum's acid have an acidic character and can be replaced by a variety of substituents by reactions with halides, aldehydes, or ketones (in a Knoevenagel condensation). Several applications of pyrolysis for the synthesis of 1,2-oxazin-6-ones and 3-hydroxypyrroles starting with Meldrum's acid were described in Section 6.2. The formation of 2-methylbenzo[*b*]thiophen-3[2H]-one starting with a derivative of Meldrum's acid is shown below [95]:



Other heterocyclic compounds can be obtained with Meldrum's acid. Preparation of a benzofuranol is shown in the following reactions [5]:



Pyrolysis of 5-(methoxymethylene)-2,2-dimethyl-1,3-dioxane-4,6-dione around 600 °C, another Meldrum acid derivative (see Section 6.2), can follow two different paths. The first path leads to methoxymethyleneketene, and the other path leads to decomposition products of methoxyacetylene. The formation of methoxymethyleneketene is shown in the following chain of reactions [96]:



Methoxyacetylene generates by decomposition a complex mixture of compounds including methylketene, ketene, formaldehyde, acetylene, ethylene, ethene, etc.

**Ascorbic acid**

Ascorbic acid, also known as Vitamin C, is (R)-3,4-dihydroxy-5-(S)-1,2-dihydroxyethyl-furan-2(5H)-one. The compound has acidic properties that are not from a carboxyl group but from an enol. Formally, ascorbic acid can be considered the  $\gamma$ -lactone of 2,3,4,5,6-pentahydroxy-2-hexenoic acid, which is a sugar acid. The fact that ascorbic acid is a sugar-type compound can be confirmed by its synthesis starting with sorbose, (3S,4R,5S)-1,3,4,5,6-pentahydroxyhexan-2-one (a keto hexose). In this synthesis, sorbose is oxidized to 2-keto-L-gluconic acid, followed by esterification with sodium methoxide when the ketone group is also transformed into an enol, and further lactonization with HCl to generate ascorbic acid.

Pyrolysis products of ascorbic acid were generated from 1.0 mg compound in a Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280^\circ\text{C}$ . The analysis of pyrolysate was done exclusively by GC/MS under conditions given in Table 4.6.1. The pyrogram is shown in Figure 19.3.1, and the peak assignment is given in Table 19.3.1 as a function of peak retention time. The relative molar content of different compounds in 100 moles of pyrolysate shown in Table 19.3.1 was obtained exclusively from the peak areas in the pyrogram. As for other pyrograms presented in this book, compounds with MW below 28 a.u. were not analyzed. Also, pyrolysis of ascorbic acid generates a considerable proportion of char, which is not accounted for as mole percent.

Pyrolysis of ascorbic acid generates compounds typical for a carbohydrate. Furfural and several furanones are among the main pyrolysis products. 2-Butenal and  $\text{CO}_2$  are also major constituents of the pyrolysate. The formation of 2-butenal associated with  $\text{CO}_2$  production is shown in the reaction below:

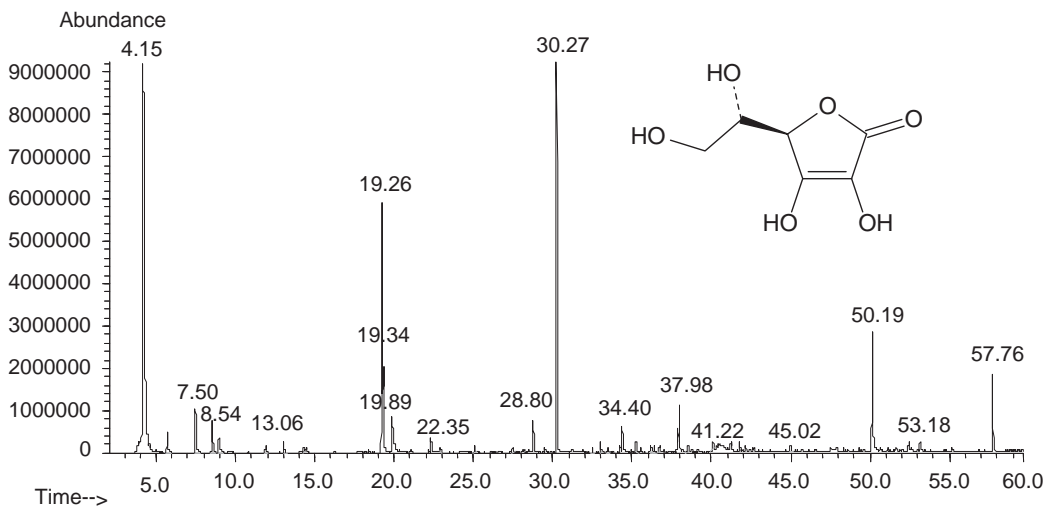
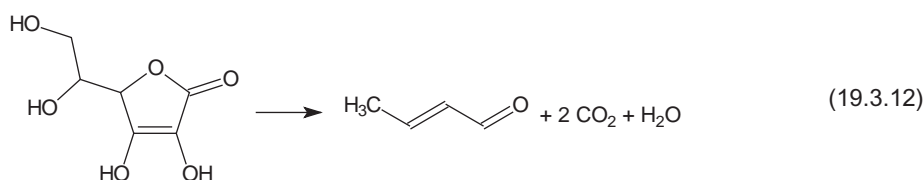


FIGURE 19.3.1. Pyrogram obtained at  $900^\circ\text{C}$  for ascorbic acid.

TABLE 19.3.1. *Peak identification as a function of retention time for the pyrogram of ascorbic acid shown in Figure 19.3.1*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.15	44	124-38-9	<b>56.66</b>
2	Formaldehyde	4.58	30	50-00-0	1.25
3	Acetaldehyde	5.71	44	75-07-0	1.21
4	Furan	7.51	68	110-00-9	1.68
5	2-Propenal (acrolein)	8.54	56	107-02-8	1.48
6	Acetone	8.99	58	67-64-1	1.03
7	2-Methylfuran	11.93	82	534-22-5	0.26
8	2,5-Dihydrofuran	13.06	70	1708-29-8	0.38
9	Methyl vinyl ketone	14.11	70	78-94-4	0.10
10	2,3-Butanedione (diacetyl)	14.32	86	431-03-8	0.14
11	Benzene	16.29	78	71-43-2	0.09
12	2-Butenal (Z)	19.26	70	15798-64-8	<b>7.95</b>
13	2-Methyl-2-propenal	19.35	70	78-85-3	2.90
14	Acetic acid	19.89	60	64-19-7	2.76
15	1-Hydroxy-2-propanone (acetol)	22.35	74	116-09-6	0.50
16	Toluene	22.94	92	108-88-3	0.12
17	Propionic acid	25.08	74	79-09-4	0.23
18	1-Hydroxy-2-butanone	27.49	88	5077-67-8	0.13
19	1,4-Dioxadiene	28.77	84	N/A	0.25
20	3-Methylcyclopentanone	28.80	98	1757-42-2	0.52
21	Furancarboxaldehyde (furfural)	30.27	96	98-01-1	<b>12.05</b>
22	Crotonic acid	31.24	86	3724-65-0	0.05
23	5-Methyl-2(3H)-furanone	31.93	98	591-12-8	0.04
24	2-Methyl-2-cyclopentene-1-one	32.52	96	1120-73-6	0.09
25	1-(2-Furanyl)ethanone	33.05	110	1192-62-7	0.19
26	2-Methyl-2-propenoic acid vinyl ester?	33.51	112	4245-37-8	0.12
27	2-Methyl-2-cyclopentene-1-one	33.81	96	1120-73-6	0.04
28	Dihydro-3-methylene-2(3H)-furanone	34.29	98	547-65-9	0.11
29	2-Hydroxy-2-cyclopenten-1-one	34.40	98	10493-98-8	0.49
30	5-Methyl-2(5H)furanone (angelica lactone)	35.27	98	591-11-7	0.24
31	Benzofuran	34.98	118	271-89-6	0.03
32	3-Methyl-2-cyclopenten-1-one	36.23	96	2758-18-1	0.12
33	Furan-2-carboxylic acid	36.41	112	88-14-2	0.15
34	2-5(H)-Furanone?	36.75	84	497-23-4	0.16
35	2H-Pyran-2-one	37.90	96	504-31-4	0.55
36	2H-Pyran-2,6(3H)-dione	37.98	112	5926-95-4	0.91
37	Phenol	38.56	94	108-95-2	0.15
38	2-Methylphenol ( <i>o</i> -cresol)	40.14	108	95-48-7	0.08
39	3,4-Epoxy-4-methyldihydro-2(3H)-furanone	40.60	114	98291-94-2	0.07
40	4-Methylphenol ( <i>p</i> -cresol)	41.22	108	106-44-5	0.09
41	3-Methylphenol ( <i>m</i> -cresol)	41.27	108	108-39-4	0.15
42	4-Methylene-1,2-dioxolan-3-one?	41.81	114	N/A	0.17

TABLE 19.3.1. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
43	Benzofuran-3-carbaldehyde?	42.18	146	N/A	0.10
44	Mixture	45.02	166	N/A	0.06
45	3,4-Dihydroxytetrahydro-2-furanone	50.19	118	N/A	<b>2.83</b>
46	Unknown	52.45	102	N/A	0.19
47	2-Deoxy-D-erythtropentose?	53.18	134	533-67-5	0.21
48	3-Hydroxy-5-(2-hydroxyacetyl)-3,5-dihydrofuran-2,4-dione	57.76	174	N/A	<b>0.90</b>

Note: Numbers in bold indicate the major pyrolysis constituents.

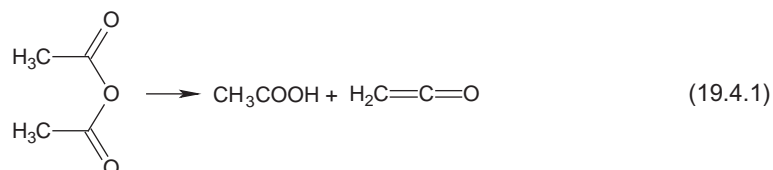
## 19.4. ORGANIC ACID ANHYDRIDES

### General aspects

Organic acid anhydrides are compounds containing two acyl groups connected to one oxygen atom and having the general formula  $R'CO-O-COR''$ . The two radicals  $R'$  and  $R''$  can be identical, different, or can be connected when the two carboxyl groups come from a dicarboxylic acid. Anhydrides can be considered as resulting from the elimination of a  $H_2O$  molecule between two  $COOH$  groups. The names of symmetric anhydrides are made by replacing the word *acid* in the name of the parent carboxylic acid with *anhydride*. For anhydrides generated from two different acids, both names of the acids are used, followed by *anhydride*.

### Anhydrides of monocarboxylic acids

Two molecules of a monocarboxylic acid can form a symmetric anhydride. The symmetric anhydride of formic acid is not known. Acetic acid anhydride thermal decomposition generates mainly ketene at temperatures as high as  $1000^\circ C$ . Since ketene also decomposes at this temperature, the reaction is typically performed by passing a rapid flow of acetic anhydride vapor over a hot platinum filament. The reaction is shown below:



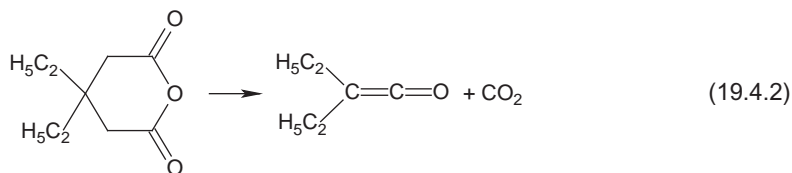
The resulting acetic acid and the ketene can further decompose, acetic acid with the formation of  $CH_4$  and  $CO_2$ , and the ketene to form  $C_2H_4$  and  $CO$ . However, rapid cooling of the reaction products may allow survival of the ketene. Several industrial procedures for the preparation of ketene were proposed following reaction 19.4.1 [97,98]. Also, a theoretical study of this reaction has been reported [99]. Thermal decomposition of diacetylsulfide was also evaluated theoretically [99]. Similar to pyrolysis of acetic anhydride, pyrolysis of propionic anhydride generates propionic acid and methylketene [96].

The first reaction during thermal decomposition of anhydrides generated from two different acids is usually the disproportionation to form two symmetrical anhydrides. These symmetrical anhydrides frequently decompose by reactions similar to 19.4.1.



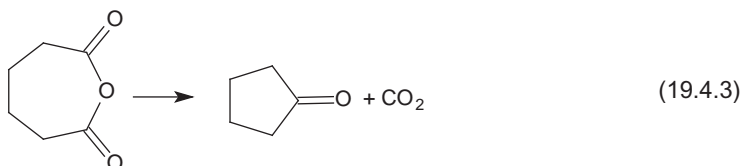
**Anhydrides of dicarboxylic acids**

Malonic acid anhydride is not a very stable compound. Diethylmalonic acid anhydride is relatively stable and at 160–180 °C decomposes to form diethylketene and CO<sub>2</sub> as shown in the following reaction:



A similar reaction is given by dimethylmalonic anhydride, but the reaction products tend to form a dimer or a polymer.

Succinic acid anhydride and glutaric acid anhydride are relatively stable molecules. Their decomposition at temperatures above 300 °C and heating time as long as 6 h generates CO<sub>2</sub> and condensation products. Adipic anhydride by pyrolysis around 240 °C generates CO<sub>2</sub> and cyclopentanone, as shown in the following reaction:



Similarly dimethyl- and trimethylpimelic anhydrides generated dimethyl and trimethyl cyclohexanones, respectively [2].

Maleic acid anhydride is also stable, and the decomposition of this compound calculated as a function of temperature for 1 s exposure time using Arrhenius equation of the form  $k = 10^{14.33 \pm 0.3} + \exp[-(60.9 \pm 1 \text{ kcal})/RT]$  is given in Figure 19.4.1 [100]. The decomposition reaction is shown below:

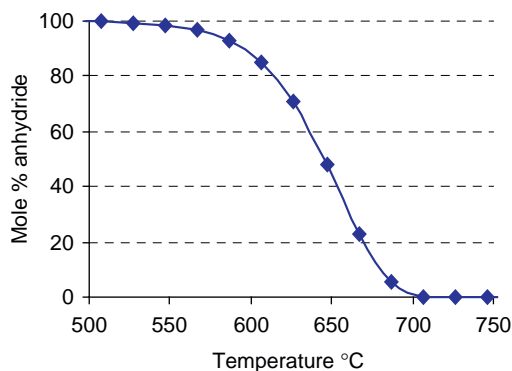
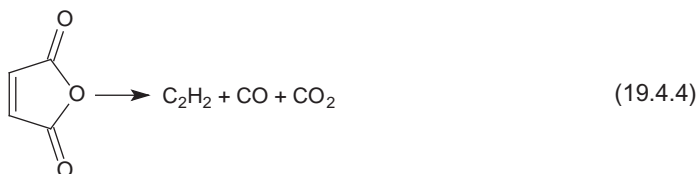


FIGURE 19.4.1. Decomposition of maleic anhydride as a function of temperature.

The reaction appears to proceed by a concerted mechanism. The reaction was studied at pressures from about 0.7 Torr to 20 Torr. No propionaldehyde or propionic acid was detected in the pyrolysate.

A condensation product is generated from phthalic anhydride when heated for 1 h at 250 °C [2].

More complex anhydrides were also studied regarding their thermal decomposition products. One example is the anhydride of dihydroabiatic acid. Pyrolysis of this compound generates CO and various decomposition products involving, besides the anhydride functionality, the rest of dehydroabiatic acid [101].

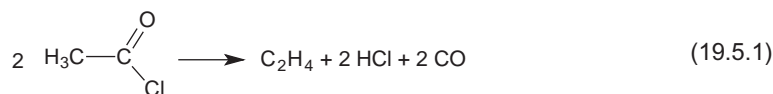
## 19.5. ACYL CHLORIDES

### General aspects

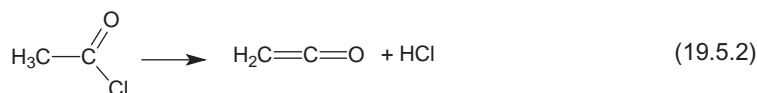
Acyl chlorides or organic acid chlorides are organic compounds with a chlorine atom bound to an acyl group. The general formula for these compounds is RCO–Cl. The radicals R can be alkyl or aryl. These compounds can be viewed as having the OH group from a carboxylic acid replaced by Cl. More complex acyl chlorides as well as compounds formed from an acyl group and another halogen are known. The name of acyl chlorides is made from the name of the acyl group (e.g., formyl, acetyl, etc.) and the word *chloride*.

### Chlorides of monocarboxylic acids

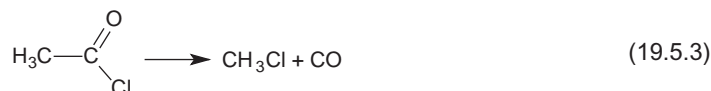
Acetyl chloride decomposes at 700–800 °C with the formation of C<sub>2</sub>H<sub>4</sub>, CO, and HCl as main pyrolysis products in a reaction as shown below:



One path for acetyl chloride decomposition starts with the formation of HCl and ketene. The reaction is shown below:



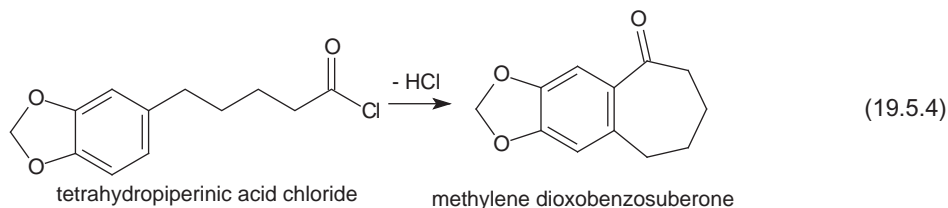
Ketene further decomposes with the formation of CO, C<sub>2</sub>H<sub>4</sub>, as well as other minor pyrolysate constituents (see Section 15.3). The kinetic parameters in Arrhenius equation for reaction 19.5.2 as reported in the literature for temperature range 242.4–350.3 °C are  $A = 10^{12.42} \text{ s}^{-1}$  and  $E^\ddagger = 69,900 \text{ kJ}$  [102]. Another path of decomposition besides reaction 19.5.2 (and further ketene decomposition) starts with the following reaction:



In the temperature range 299–491 °C, methyl chloride can be identified in the pyrolysate, and the compound decomposes at higher temperatures with the formation of C<sub>2</sub>H<sub>4</sub> and HCl (see Section 8.1).

Other acyl chlorides follow one or the other of the two paths. For example, palmityl chloride, lauryl chloride, and pelargonyl chloride (nonanoic acid chloride) decompose with the formation of HCl and the corresponding ketene. On the other hand, triphenyl acetyl chloride generates CO and triphenylchloromethane. Some other compounds decompose following both mechanisms (e.g., diphenylacetyl chloride).

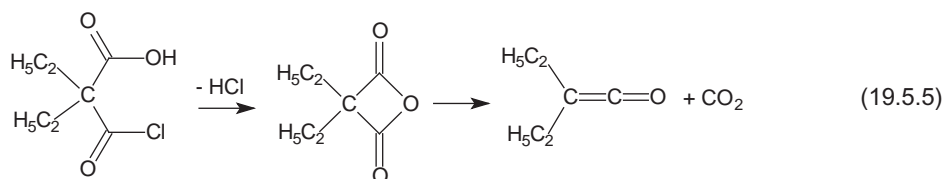
In some compounds, the elimination of HCl takes place from a different hydrogen than the  $\alpha$ -carbon to the COCl group. This is shown below for a reaction in which a stable cycle is also generated [103]:



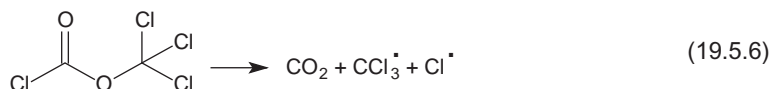
Pyrolysis of more complex acyl chloride molecules usually involves decomposition of the whole molecule. One example is the pyrolysis of dehydroabiatic acid chloride, which when pyrolyzed at 450 °C on a Vycor rod generates a mixture of products such as 19-norabieta-4,8,11,13-tetraene, 19-norabieta-4(18),8,11,13-tetraene, 19-norabieta-3,8,11,13-tetraene, and *cis*-1,10a-dimethyl-7-isopropyl-1,2,3,9,10,10a-hexahydro-phenanthrene [101].

### Chlorides of dicarboxylic acids and carbonic acid

Acyl chlorides are also known for dicarboxylic acids. Oxalyl chloride, for example, is prepared from oxalic acid and  $\text{PCl}_5$ , similar to other acyl chlorides. Pyrolysis of this compound at 600 °C generates phosgene and CO [2]. Pyrolysis of monoacid chloride of diethylmalonic acid was also studied [2], and this decomposition leads to the formation of diethylketene by the following reaction:



A number of acyl chlorides are derived from carbonic acid. The simplest of these is phosgene,  $\text{COCl}_2$ . Phosgene decomposition takes place with the formation of CO and  $\text{Cl}_2$  at temperatures above 350–400 °C [104]. The reaction mechanism involves the formation of free radicals  $\text{Cl}^\bullet$  and  $\text{COCl}^\bullet$ , followed by several propagation reactions. Kinetic parameters for phosgene decomposition are reported in the literature [105]. Diphosgene (trichloromethyl chloroformate) decomposition also involves formation of free radicals, as shown in the following first step of pyrolysis:



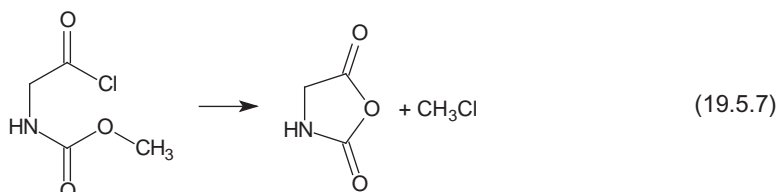
Kinetic parameters for this decomposition are reported [105]. Thermal decomposition of isopropyl chloroformate was also studied. In the temperature range 229–277 °C, this compound generates  $\text{CO}_2$ , HCl, and propene in a reaction of the first order with Arrhenius equation  $k = 10^{13.94} \exp[-174000 \text{ (J)/} RT] \text{ s}^{-1}$  [106].

### Acyl chlorides with additional functionalities

Several studies were performed on pyrolysis of compounds resulting from dicarboxylic acids with one carboxyl transformed into an acid chloride and the other having an ester group. Some decompositions of these molecules lead to the formation of an anhydride with the elimination of an alkyl chloride

(when the half ester is formed with an alcohol). Other reactions take place with disproportionation and formation of an anhydride and a dichloride, and some reactions occur with both paths. For example, succinyl chloride monoethyl ester decomposes around 115 °C to form ethyl chloride and succinic anhydride and also with the formation of ethyl succinate and disuccinyl chloride.

Carbamyl chlorides were also studied. For example, 2-(methoxycarbonylamino)acetyl chloride or carbomethoxyglycyl chloride decomposes at mild heating as shown in the following reaction:



Other carbamyl chlorides decompose differently. For example, phenylcarbamyl chloride generates by heating HCl and phenyl isocyanate [2].

## 19.6. AMIDES AND IMIDES

### General aspects

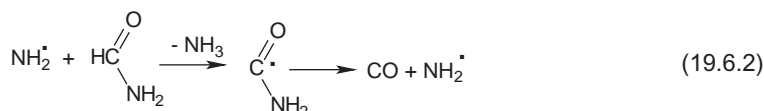
Amides (primary amides) are derivatives of organic acids R<sup>1</sup>-COOH in which the -OH group from the carboxyl is replaced with the group NH<sub>2</sub>. Primary amides can also be viewed as replacing one hydrogen from ammonia with an acyl group. The hydrogen atoms from the amide group can be replaced further with hydrocarbon radicals (alkyl or aryl), generating substituted amides. The NH<sub>2</sub> hydrogens from an amide can also be replaced with other acyl groups to form secondary amides or tertiary amides. Cyclic secondary amides are known as imides. The naming of amides is done using the name of the acyl radical and the name *amide* (e.g., CH<sub>3</sub>-CONH<sub>2</sub> is acetyl amide or acetamide).

### Simple amides

Formamide decomposes starting around 180 °C following two decomposition routes, as shown in the following reactions:



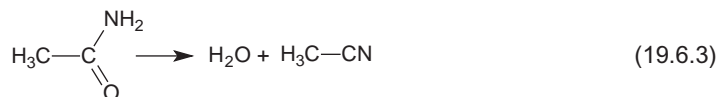
At higher temperatures the formation of CO and NH<sub>3</sub> is the main path, with the cleavage of the C-N bond and formation of NH<sub>2</sub><sup>•</sup> and HCO<sup>•</sup> free radicals. These free radicals continue the decomposition reaction as shown below:



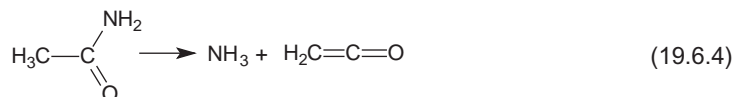
Photolytic decomposition of formamide at temperatures between 262 °C and 500 °C at partial vapor pressures of formamide from 6 Torr to 33 Torr in an inert gas has been studied, and the Arrhenius parameters for the decomposition are reported in the literature [107]. The decomposition of formamide

in the presence of atomic hydrogen at 275 °C when the main decomposition product is HCN has also been reported [108].

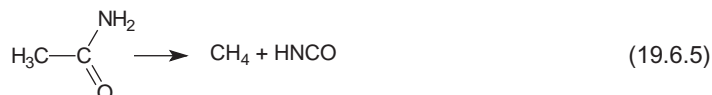
Acetamide vapors decomposes around 400 °C following the main path shown below:



This reaction is favored by the contact with active surfaces such as alumina, glass, graphite, etc. Besides reaction 19.6.3, the formation of  $\text{NH}_3$  and ketene also occurs as shown in the following reaction:



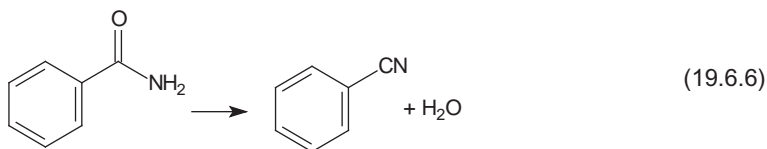
A third reaction was also detected in acetamide decomposition, leading to the formation of  $\text{CH}_4$  and isocyanic acid as shown below:



The pyrolysis products of acetamide have the capability to react, and the resulting compounds may undergo further pyrolytic decompositions (e.g., decomposition of  $\text{NH}_4\text{NCO}$ , decomposition of ketene, etc.).

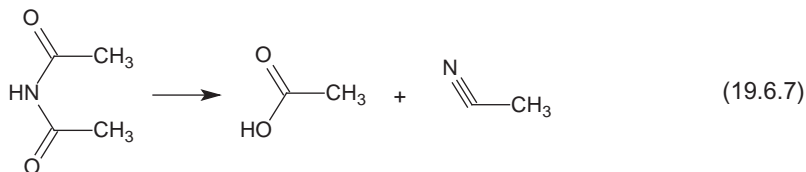
The amides of propionic acid, butyric acid, isobutyric acid, isovaleric acid, and caproic acid decompose around 400 °C mainly by reactions similar to 19.6.3 and generate nitriles [109,110].

Simple aromatic amides decompose mainly with the formation of nitriles as well. Around 425 °C, pyrolysis of benzamide generates with high yields benzonitrile, as shown in the following reaction:



### Secondary and tertiary amides

The replacement of two hydrogens from an ammonia molecule with acyl groups leads to the formation of secondary amides. One example of a secondary amide is diacetamide. This compound decomposes at 250 °C and 2 h heating following a disproportionation type reaction as shown below:

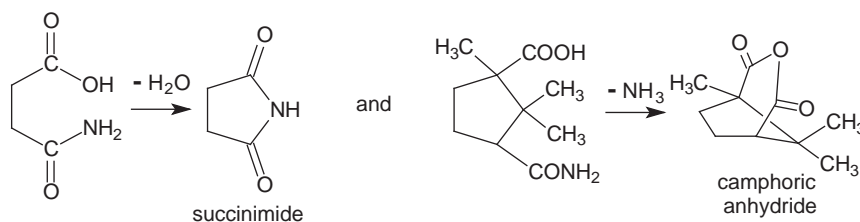


The pyrolysate also contains some acetamide. Dibenzamide, which is transformed into benzoic acid and benzonitrile [2], behaves similar to diacetamide. Di-*p*-toluylamide also generates at heating the corresponding nitrile and *p*-toluic acid. Tertiary amides are very stable to heating. Tribenzamide does not decompose until about 400 °C.

**Amides of dicarboxylic acids**

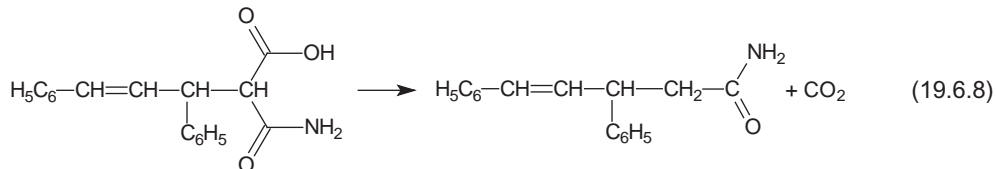
Dicarboxylic acids have the capability to generate monoamides in which only one COOH group is replaced by CONH<sub>2</sub>, diamides where both carboxyl groups are transformed into primary amides, and imides, which are cyclic secondary amides formed by the replacement of two OH groups from the carboxyls with one bidentate NH group (imides pyrolysis is discussed in the next subsection).

Typical thermal decomposition of monoamides of dicarboxylic acids occurs in a manner analogous to the decomposition of dicarboxylic acids. When the formation of a stable cycle is possible (see Section 17.2), the pyrolysis usually generates either imides or anhydrides, depending on the molecule structure [111]. Two different examples are shown below:

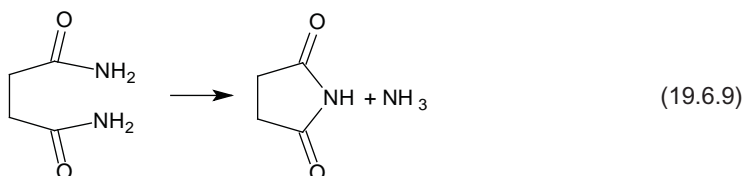


Phthalic acid monoamide as well as substituted phthalic acid monoamide generate the corresponding imide by thermal decomposition.

When a cycle formation is not feasible due to steric constraints, the decomposition takes place by different paths, usually with the elimination of CO<sub>2</sub> from the carboxyl group. As an example, a monoamide of a derivative of malonic acid decomposes around 165 °C as shown below [2]:



The same trend as for the decomposition of dicarboxylic acids is seen for the decomposition of diamides. In the case of diamides, where formation of a stable cycle is not possible, the decomposition leads to a mixture of products. Oxalic acid diamide, for example, decomposes with the formation of NH<sub>3</sub>, CO, HCN, urea, and NH<sub>4</sub>OCN (ammonium cyanate). On the other hand, the diamide of succinic acid (succinamide) generates by thermal decomposition around 200 °C mainly succinimide, as shown in the following reaction:



Similarly, phthalic acid diamide (phthalamide) changes easily into phthalimide by elimination of NH<sub>3</sub>, and maleic acid diamide changes into maleimide. The formation of stable five-atom cyclic imides explains the reactions in the case of the diamides of succinic, maleic, and phthalic acids.

A diamide can also be generated from adipic acid (adipamide). This compound would produce by pyrolysis a seven-atom cycle, when it would follow a reaction similar to 19.6.8. However, the stability of a seven-atom cycle is not as high as that of five- or six-atom cycles, and adipic acid diamide generates more than one major pyrolysis product. An experiment was performed on adipic acid diamide starting

with 1.0 mg sample and in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900\text{ }^{\circ}\text{C}$ ,  $\beta = 10\text{ }^{\circ}\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280\text{ }^{\circ}\text{C}$ . The analysis of the pyrolysate was performed under conditions given in Table 4.6.1. The pyrogram for adipic acid diamide is shown in Figure 19.6.1. The compound identifications and their relative molar content in 100 moles of pyrolysate are given in Table 19.6.1. The identification in the pyrolysate of the expected adipimide (azaperhydroepine-2,7-dione) was done tentatively based on the mass spectrum shown in Figure 19.6.2.

As shown in Table 19.6.1, the adipimide (azaperhydroepine-2,7-dione) is not the main pyrolysis product of adipic acid diamide, but it is present at relatively high levels. This compound is generated by the following reaction:

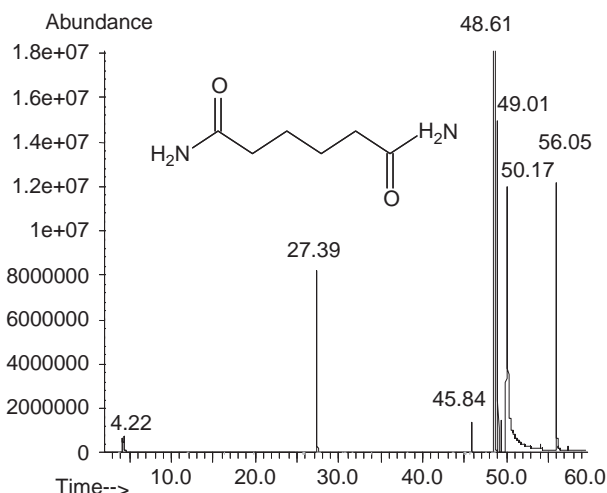
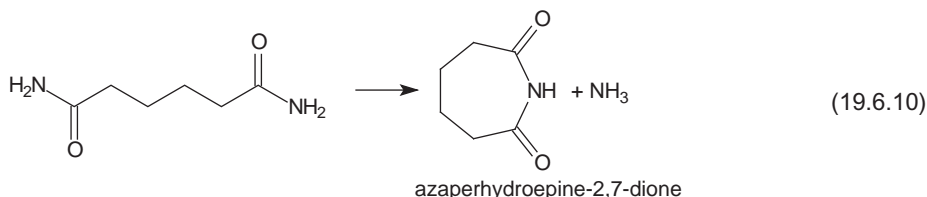


FIGURE 19.6.1. Pyrogram obtained at  $900\text{ }^{\circ}\text{C}$  for adipamide ( $\text{MW} = 144$ ).

TABLE 19.6.1. Peak identification as a function of retention time for the pyrogram of adipamide shown in Figure 19.6.1 ( $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ , and  $\text{N}_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.30	44	124-38-9	3.37
2	Cyclopentanone	27.39	84	120-92-3	<b>6.80</b>
3	6-Methyl-3-pyridinol	45.84	109	1121-78-4	0.82
4	Hexanedinitrile	48.61	108	111-69-3	<b>36.03</b>
5	Azaperhydroepine-2,7-dione	49.01	127	N/A	<b>9.94</b>
6	2-Imino-cyclopentanecarbonitrile	49.37	108	2321-76-8	0.85
7	5-Cyanopentanoic acid	50.17	127	5264-33-5	<b>30.55</b>
8	5-Cyanopentanamide	56.05	126	N/A	<b>11.64</b>

Note: Numbers in bold indicate the major pyrolysis constituents.

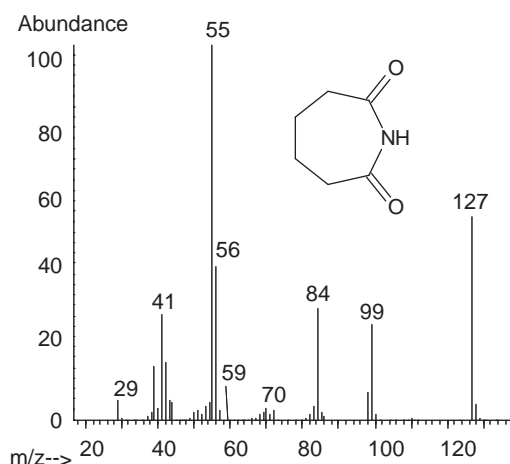
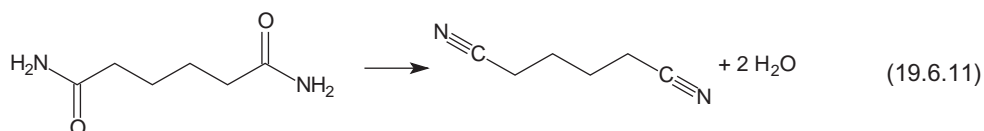


FIGURE 19.6.2. Mass spectrum of (tentatively) azaperhydroepine-2,7-dione.

The identification of azaperhydroepine-2,7-dione was done only tentatively since its mass spectrum is not available in common mass spectral libraries (see Figure 19.6.2).

The main pyrolysis product of adipic acid diamide is hexandinitrile, which is generated in a reaction as shown below:



Partial dehydration with the elimination of only one water molecule generated 5-cyanopentanamide, also present in the pyrogram at relatively high level.

Another major component of pyrolysis of adipic acid diamide is 5-cyano adipic acid (5-cyanopentanoic acid). This compound has one amide group hydrolyzed to acid and the other group changed into a nitrile by water elimination. The formation of 5-cyano adipic acid may take place by various paths. One possibility is the hydrolysis of one amide group from the initial adipic acid diamide into an acid and the elimination of water from the remaining amide group. Another alternative is the formation of a dinitrile that is further hydrolyzed at one nitrile group to acid. Other paths are also possible such as formation of the (cyclic) adipimide (azaperhydroepine-2,7-dione) followed by a rearrangement.

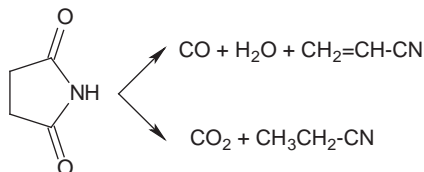
### Imides

Imides are typically more stable to heating as compared to amides. As previously shown, several diamides by pyrolysis in the temperature interval 400–450 °C generate imides. Since imides are usually stable and higher temperatures are required for their decomposition, the paths followed in the process are a function of the imide molecular structure. Maleimide decomposition, for example, takes place with molecular fragmentation and generation of CO, C<sub>2</sub>H<sub>2</sub>, HNCO, oxazole, etc. A theoretical study on this reaction has been reported [112].

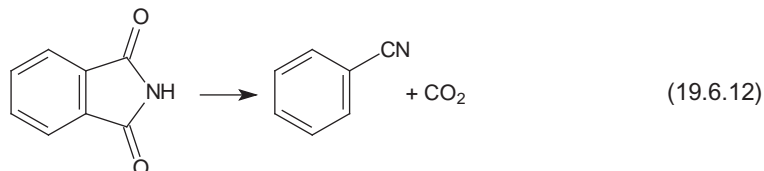
Other imides decomposition takes a different route. Succinimide pyrolyzed in the temperature range 425–500 °C decompose with the opening of the ring. The main pyrolysis products are CO, H<sub>2</sub>O, CH<sub>2</sub>=CH-CN, CO<sub>2</sub>, and CH<sub>3</sub>CH<sub>2</sub>CN [113]. The formation of these compounds is shown in the



following reactions:



Phthalimide heated around 480 °C generates benzonitrile, as shown in the following reaction:

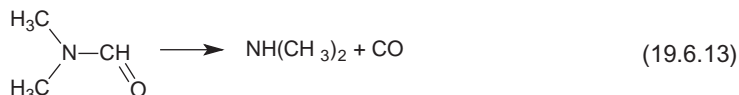


The same route is taken by phthalimide with chlorine substituents at the aromatic ring. 4-Chlorophthalimide decomposes above 500 °C, and tetrachlorophthalimide decomposes around 600 °C [114].

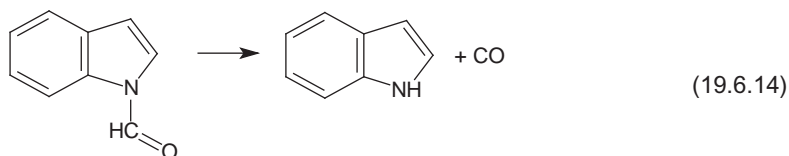
#### Amides substituted at the nitrogen atom

Primary amides, secondary amides, and imides can be substituted at the nitrogen with alkyl or aryl radicals. The resulting compounds are known as *N*-substituted amides (or *N*-substituted imides). The nature of *N*-substituent and that of the acyl radical influence the pyrolysis outcome.

*N*-substituted formamides have the general tendency to eliminate CO and produce amine. For example, dimethylformamide above 350 °C generates CO and dimethylamine by the following reaction:

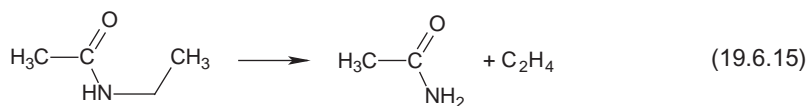


The same type of reaction with CO elimination takes place for more complex molecules such as *N*-formylindole, which decomposes above 300 °C and generates indole by the following reaction:



*N*-substituted acetamides do not have the capability to eliminate CO easily and are more stable to decomposition. For example, the decomposition of *N*-acetylindole takes place at higher temperatures than those for *N*-formylindole, with the formation of various fragments, CO, low levels of quinoline, etc.

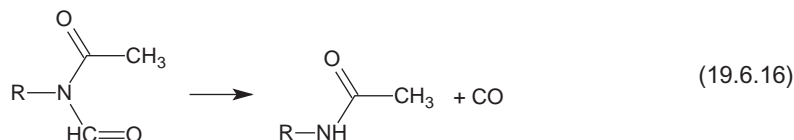
Dimethylacetamide decomposes only above 450–500 °C, generating H<sub>2</sub>O, NH<sub>3</sub>, and other fragment molecules. However, decomposition of ethyl acetamide takes place at lower temperatures and mainly by the following reaction [115–117]:



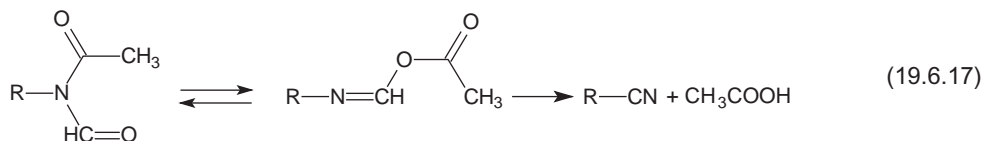
This reaction is similar to that of ester thermal decomposition when a  $\beta$ -hydrogen is available at the alcohol substituent and has some generality for amides. When  $\beta$ -hydrogens are not available, the reaction takes place with more fragmentation. In the cases of a  $\beta$ -hydrogen present in a double bond or involved in an aromatic structure, reactions similar to 19.6.15 are not characteristic.

A common substituted acetamide is *N*-phenylacetamide or acetanilide. This compound has applications as an intermediate in various organic syntheses and was used as an antipyretic drug until *N*-(4-hydroxyphenyl)acetamide (acetaminophen or Tylenol<sup>®</sup>) was proven much less toxic. Acetanilide is stable up to about 400 °C, and above this temperature it decomposes, generating a mixture of compounds including aniline, acetic acid, *o*-aminoacetophenone, and acetodiphenylamine [114].

For substituted diamides several *N*-formylacetamides were evaluated, including *N*-phenyl, *N*-*n*-butyl, *N*-*sec*-butyl, and *N*-cyclohexyl-*N*-formylacetamide. The main reaction during pyrolysis is the decarbonylation process, which takes place as shown below:

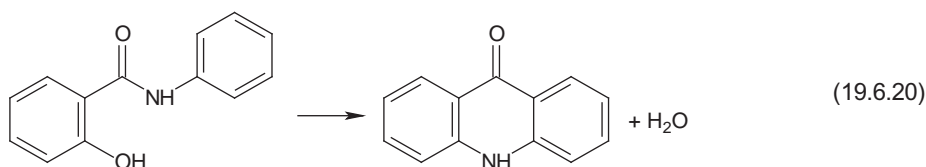
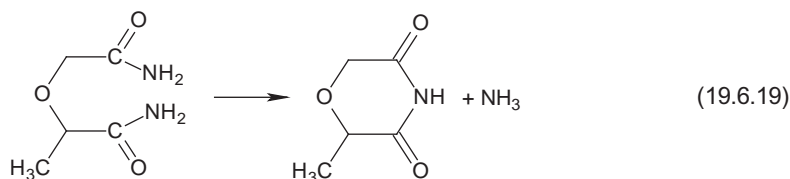
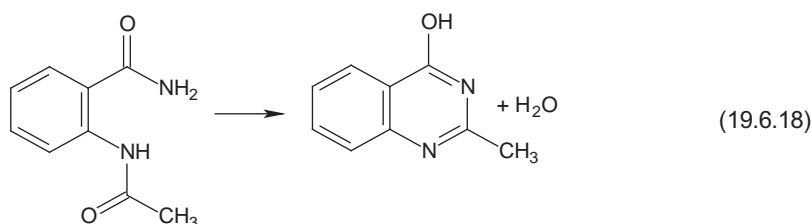


However, depending of the nature of the radical R, an equilibrium imide/isoimide was found possible [118]. The result of this type of equilibrium during pyrolysis leads to the formation of nitriles, as shown in the following reaction:

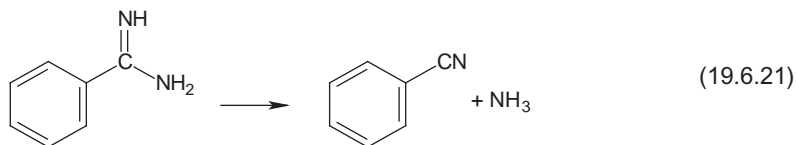


### Amides and substituted amides with additional functional groups

The presence of other functional groups in an amide molecule may influence the pyrolysis outcome, particularly when stable heterocyclic compounds are formed. A few such reactions are shown as follows [2]:



Several other compounds related to amides are known, such as haloamides and haloimides. The Na salt of a bromoamide decomposes by heating to form isocyanates [2]. Amidines are also related to amides, by replacement in the formula of an amide the C(=O) group with C(=NH). Amidines generate by thermal decomposition nitriles and NH<sub>3</sub>, as shown below for benzamidine:

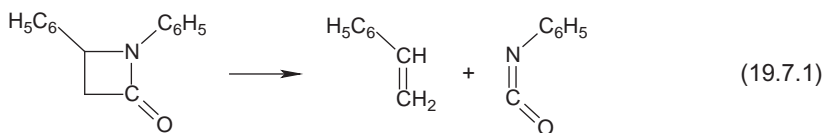


## 19.7. LACTAMS

### General aspects

Lactams are internal amides, which can be viewed as formed by water elimination between the COOH group and the NH<sub>2</sub> group present on the same molecule. Similar to the case of lactones (formed between a COOH and an OH group), lactams are easily generated when a five-atom ring ( $\gamma$ -lactams) or a six-atom ring ( $\delta$ -lactams) is formed. Other lactams ( $\beta$ ,  $\epsilon$ , etc.) are also known, but the  $\alpha\beta$ -lactams are not formed as a result of thermal elimination of water between COOH and NH<sub>2</sub> from the same molecule.

The decomposition of a  $\beta$ -lactams can be exemplified by the decomposition of  $\beta$ -anilino- $\beta$ -phenylpropionic lactam, which decomposes at 600 °C into styrene and phenylisocyanate:



The lactams with five- and six-atom rings ( $\gamma$ - and  $\delta$ -lactams) are very stable to temperatures up to 450–500 °C. The decomposition takes place with the formation of numerous fragments. Special attention was given to  $\epsilon$ -caprolactam thermal decomposition, particularly related to the recovery of this compound from Nylon-6 scrap [119]. At temperatures above 600 °C,  $\epsilon$ -caprolactam decomposes with the formation of various fragments including NH<sub>3</sub>, hexenoic acid, CO<sub>2</sub>, and char. *N*-substituted derivatives of  $\epsilon$ -caprolactam were also evaluated regarding their thermal behavior [120].

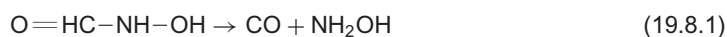
## 19.8. HYDROXAMIC ACIDS AND HYDRAZIDES

### General aspects

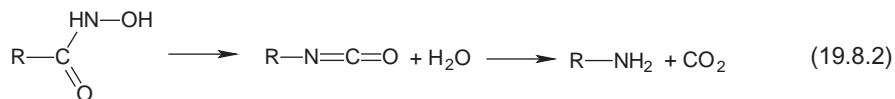
When an acyl group replaces a hydrogen from hydroxylamine, a compound known as hydroxamic acid is generated. Hydroxamic acids are weak acids, their character not being caused by an organic carboxyl. The replacement of a hydrogen from hydrazine with an acyl group leads to the formation of hydrazides.

### Hydroxamic acids

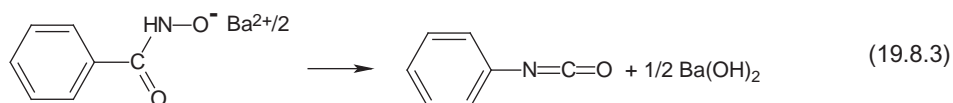
The general formula of hydroxamic acids is R-C(=O)NHOH. A tautomeric structure of hydroxamic acids is that of hydroximic acid R-C(OH)=NOH. Formohydroxamic acid decomposes at mild heating (80 °C) to generate CO and hydroxylamine, as shown in the following reaction:



Hydroxamic acids other than those of formic acid, upon heating, can lose water and transform into isocyanates. The resulting isocyanate hydrolyzes and generates  $\text{CO}_2$  and an amine in a reaction as shown below:

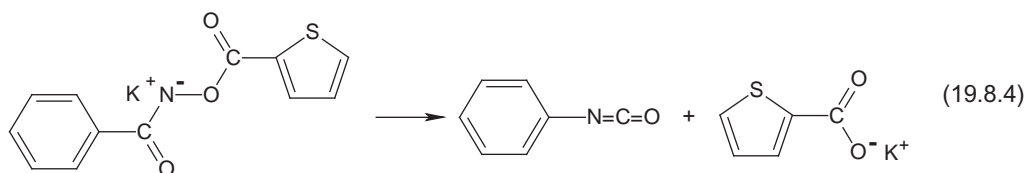


The isocyanate can be isolated if a metal salt of a hydroxamic acid is decomposed by heat, as shown for benzohydroxamic acid barium salt [121,122]:



In this reaction, the aryl group migrates from the carbon atom to the nitrogen, and this reaction is known as Lossen rearrangement. Anisylhydroxamic acid and *p*-toluyl-hydroxamic acid behave similarly.

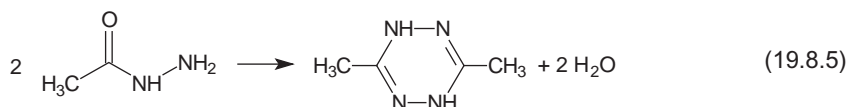
Dihydroxamic acids give the same reaction as hydroxamic acids, generating an isocyanate as shown in the following reaction for the thiophene carboxy derivative of benzohydroxamic acid [123]:



A similar reaction is given by the acetyl derivative of benzohydroxamic acid which generates phenyl isocyanate and acetic acid. Trihydroxamic acids are also known and their pyrolysis leads to isocyanates formation [2].

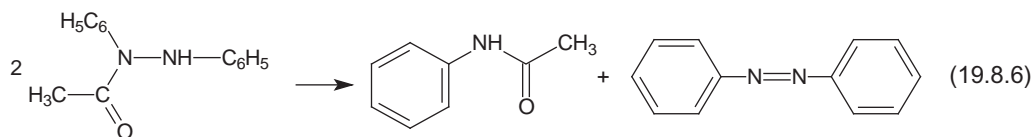
### Hydrazides

Hydrazides are compounds containing the group  $\text{>C(O)-NH-N<}$  where the hydrazine moiety  $\text{>N-N<}$  is attached to an acyl group. Acetyl hydrazide decomposes at relatively low temperature ( $180^\circ\text{C}$ ) when heated for extended period of time, eliminating water in a reaction as shown below:

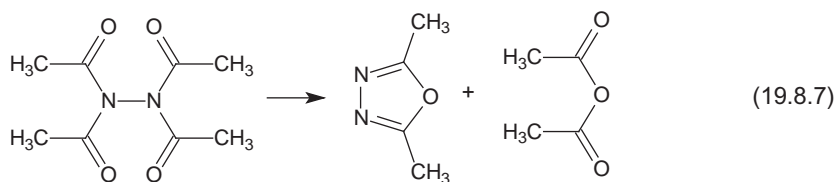


A similar reaction is known for formyl phenylhydrazide, which generates diphenyl-dihydropyridazine when heated at  $210^\circ\text{C}$  [2]. Other hydrazides are relatively stable compounds, one example being maleic hydrazide [124], which can be transferred from the tobacco section of a cigarette into smoke without being pyrolyzed. The compound has a heterocyclic structure and can be considered a 1,2-dihydropyridazine-3,6-dione. Its decomposition at temperatures above  $550^\circ\text{C}$  takes place with the molecule fragmentation and formation of  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{NO}$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ , etc.

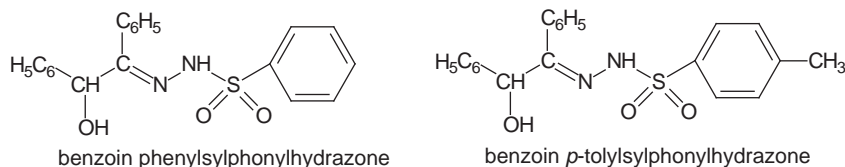
Depending on the molecular structure, some hydrazides pyrolyze in different manners. For example, acetyl hydrazobenzene decomposes with the formation of *N*-phenylacetamide (acetanilide) and azobenzene, as shown in the following reaction:



Tetraacetyl hydrazide around  $350^\circ\text{C}$  follows a different path and generates a heterocycle (dimethylfurodiazole), as shown in the following reaction:



Two other hydrazine derivatives that have been studied regarding their thermal degradation products are benzoin phenylsulfonylhydrazone and benzoin *p*-tolylsulfonylhydrazone [125]. These compounds can be considered either a hydrazone of benzoin or a hydrazide of an arylsulfonic acid and are shown below:



Thermal degradation at  $200^\circ\text{C}$  of benzoin phenylsulfonylhydrazone, for example, generates numerous products such as  $\text{NH}_3$ , benzoic acid (4%), benzophenone (6.1%), bibenzyl (6.5%), aniline (5.2%), diphenyl acetylene (6%), deoxybenzoin (3.6%), *N*-benzylbenzylamine (4.5%), diphenyldisulfide (7.8%), diphenylthiosulfone, *S*-phenylthiobenzoate, benzenesulfonamide (2.5%), 2-phenylindole (6.6%), 2,3,4,5-tetraphenylfuran (8.6%), 2,4,5-triphenylimidazole (11%), and 2,4,5-triphenyloxazole (10.2%). Pyrolysis of these compounds starts with the typical cleavage of the N–N bond and formation of free radicals. Due to the complexity of the molecule, there are possible various further reactions caused by the free radicals, including radical rearrangements,  $\text{SO}_2$  extrusion, hydrogen shifts, etc.

## 19.9. NITRILES AND ISOCYANIDES

### General aspects

Nitriles are compounds with the general formula  $\text{R}-\text{C}\equiv\text{N}$ , where R is an organic radical. The name of nitrile is made from that of the acid radical with the same number of carbons and the word *nitrile* (e.g.,  $\text{CH}_3-\text{CN}$  is acetonitrile). The name of the radical followed by *cyanide* is sometimes used (not the IUPAC recommendation). Isocyanides (also called isonitriles) have the general formula  $\text{R}-\text{N}^+ \equiv \text{C}^-$ .

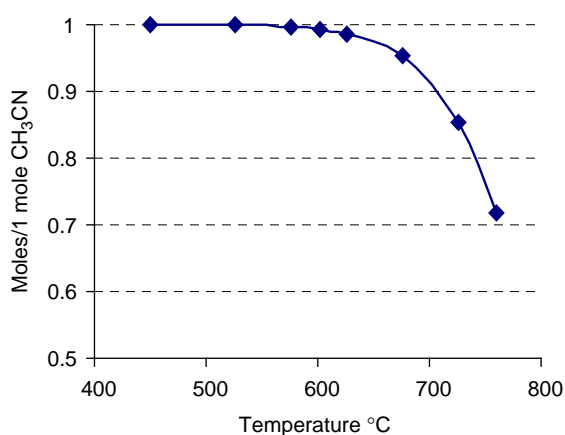


FIGURE 19.9.1. Calculated decomposed moles of acetonitrile for 13.5 min contact time at different temperatures [126].

TABLE 19.9.1. Model reactions for acetonitrile pyrolysis [126]

Initiation reaction	Propagation reaction	Termination reaction
$\text{CH}_3\text{CN} \rightarrow \text{H}^\bullet + \text{CH}_2^\bullet\text{CN}$	$\text{H}^\bullet + \text{CH}_3\text{CN} \rightarrow \text{HCN} + \text{CH}_3^\bullet$	$\text{H}^\bullet + \text{CH}_2^\bullet\text{CN} \rightarrow \text{CH}_3\text{CN}$
	$\text{CH}_3^\bullet + \text{CH}_3\text{CN} \rightarrow \text{CH}_4 + \text{CH}_2^\bullet\text{CN}$	$\text{CH}_3^\bullet + \text{H}^\bullet \rightarrow \text{CH}_4$
	$\text{CH}_2^\bullet\text{CN} + \text{CH}_3\text{CN} \rightarrow \text{HCN} + \text{CH}_3\text{CH}^\bullet\text{CN}$	$\text{CH}_3^\bullet + \text{CH}_2^\bullet\text{CN} \rightarrow \text{CH}_3\text{CH}_2\text{CN}$
	$\text{CH}_3\text{CH}^\bullet\text{CN} \rightarrow \text{HCN} + \text{C}_2\text{H}_3^\bullet$	
	$\text{CH}_3\text{CH}^\bullet\text{CN} \rightarrow \text{CH}_2=\text{CHCN} + \text{H}^\bullet$	
	$\text{C}_2\text{H}_3^\bullet + \text{CH}_3\text{CN} \rightarrow \text{C}_2\text{H}_4 + \text{CH}_2^\bullet\text{CN}$	
	$\text{C}_2\text{H}_3^\bullet + \text{CH}_3\text{CN} \rightarrow \text{CH}_2=\text{CHCN} + \text{CH}_3^\bullet$	
	$\text{C}_2\text{H}_3^\bullet \rightarrow \text{C}_2\text{H}_2 + \text{H}^\bullet$	

### Aliphatic nitriles

Acetonitrile pyrolysis was reported for a study performed in a flow reactor where the acetonitrile vapors were passed through a quartz plug-flow reactor at 1 atm pressure with temperatures in the range 723–1033 K [126]. The main pyrolysis products generated from acetonitrile were  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , HCN, and  $\text{CH}_2=\text{CH}-\text{CN}$ . The decomposition of acetonitrile calculated for a contact time of 13.5 min at different temperatures is shown in Figure 19.9.1. The calculation was done based on Arrhenius equation of the form reported to have the expression  $k (\text{s}^{-1}) = 10^{6.22} \exp[-190 (\text{kJ/mol})/RT]$ .

The mole ratio of the main reaction products at 759.85 °C and 13.5 min contact time was as an average 71.6 mol%  $\text{CH}_3\text{CN}$  (undecomposed), 18.1 mol%  $\text{CH}_4$ , 10.0 mol% HCN, and 0.225 mol%  $\text{C}_2\text{H}_4$ .

The decomposition of acetonitrile is likely to start with the cleavage of a C–H bond, since the C–N bond has a dissociation energy of about 123.6 kcal/mol [127] (or 110.2 kcal/mol in Table 3.1.2), and the C–H bond has a dissociation energy of 93 kcal/mol. The main initiation, propagation, and termination reactions in acetonitrile decomposition are listed in Table 19.9.1. Although  $\text{H}^\bullet$  atoms are assumed to be formed in these reactions, molecular hydrogen was not detected among the pyrolysis products of acetonitrile.

In addition to acetonitrile, other aliphatic nitriles were studied regarding their pyrolysis. These include acrylonitrile, propionitrile, and methacrylonitrile [126]. The pyrolysis was performed for these compounds in flash mode at 950 °C, 20 s heating time. The main pyrolysis products of these nitriles are shown in Table 19.9.2. Acetonitrile was found to be more stable to heating than the other nitriles.

Other studies on thermal decomposition of aliphatic nitriles are reported in the literature [128–132].

TABLE 19.9.2. *Estimated levels of various pyrolysis products at 950 °C in flash pyrolysis of several aliphatic nitriles [126]*

Compound	Acetonitrile	Acrylonitrile	Propionitrile	Methacrylonitrile
CH <sub>4</sub>	***	**	**	**
C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>2</sub>	**	***	***	**
C <sub>2</sub> H <sub>6</sub>	*	*		
HCN	***	***	***	**
C <sub>3</sub> H <sub>6</sub>	*	*		
CH <sub>3</sub> CN	Not included	***	**	**
C <sub>2</sub> H <sub>3</sub> CN	*	Not included	***	***
C <sub>2</sub> H <sub>5</sub> CN		*	Not included	*
Methacrylonitrile				Not included
Crotononitrile		*		
Benzonitrile		**		

\*Minor product.

\*\*Moderate product.

\*\*\*Major product.

### Benzonitrile

Benzonitrile is a stable compound to pyrolysis, and its decomposition starts above 550 °C with very low decomposition rate. A study performed in a flow reactor on N<sub>2</sub> saturated with benzonitrile [133] in the temperature range 550–600 °C showed that the main pyrolysis products of this compound are HCN, benzene, monocyanodiphenyls, dicyanodiphenyls, and dicyanobenzenes, as well as char. The reaction takes place by a radicalic mechanism, starting with the following initiation reaction:



The position of the hydrogen atom where the cleavage takes place is not preferential, since pyrolysis generates a mixture of monocyanodiphenyls, dicyanodiphenyls, and dicyanobenzenes (e.g., 2-cyano, 3-cyano, and 4-cyanobiphenyl). The presence of dicyanobenzene in the pyrolysate indicates that free CN<sup>•</sup> radicals are likely to be formed in the reaction. Kinetic parameters for the reactions of benzonitrile decomposition are reported in the literature [133], the formation of different compounds having different reaction orders. The pyrolysate at 575 °C obtained for 30 min contact time contains about 5.9 mol% HCN, 4.9 mol% dicyanobenzenes, 3.0 mol% benzene, 1.2% monocyanobiphenyls, and the other compounds at lower levels.

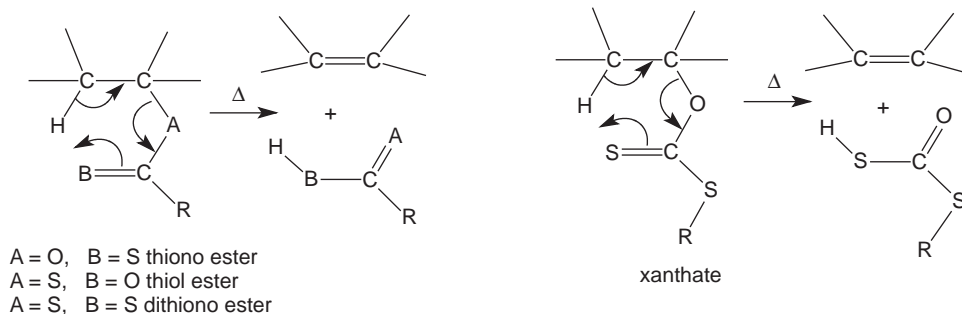
## 19.10. THIOESTERS AND THIOAMIDES

### General aspects

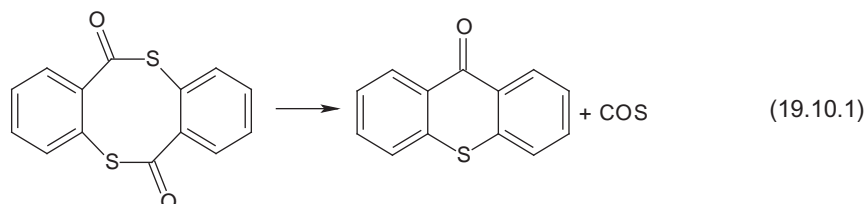
Thioesters are esters having in their formula one or two of the oxygen atoms replaced by sulfur atoms. These include thiol esters RC(=O)SR', thiono esters RC(=S)OR', and dithiono esters RC(=S)SR'. Also, substitution of two sulfur atoms in carbonates generates an important group of compounds known as xanthates. Thioamides are compounds with the general formula R-C(=S)NH<sub>2</sub>. The hydrogen atoms from thioamides can be replaced by organic radicals to generate substituted thioamides.

### Thioesters

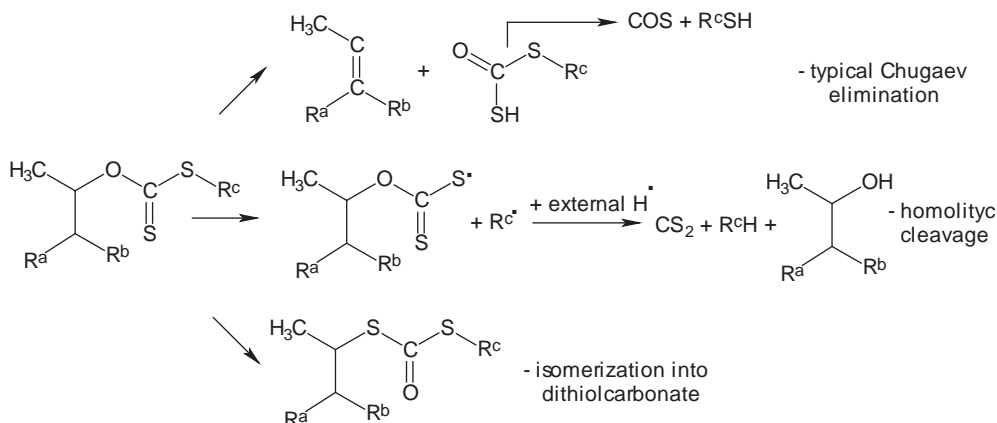
Thermal decomposition of thioesters is similar to that of the normal esters.  $\beta$ -Elimination reactions for thiono esters, thiol esters, and xanthates were described in Section 2.2:



The efficiency of  $\beta$ -elimination reactions for thioesters depends on the specific compound pyrolyzed, and the yield for the  $\beta$ -elimination can vary considerably [134]. Also, further reactions may continue after the initial step of the elimination. As an example, thionacetates generate an alkene, but only thiolacetic acid is found in the pyrolysate together with some undecomposed thiolacetate [135]. Some other pyrolysis results described in the literature include that of *S*-butyl thioacetate [136], acetyl thiosalicylic acid [2], dithio-disalicide [137], etc. Pyrolysis of thiosalicylic acid generates acetic acid among other pyrolysis products. The double ester dithio-disalicide decomposes with the formation of a heterocycle, as shown in the following reaction:



Xanthates pyrolysis has been used with success to prepare alkenes from alcohols. The alcohols can be easily transformed into xanthates by treatment with  $\text{CS}_2$  in the presence of a strong base (e.g., NaOH) followed by the treatment with an alkylating reagent (e.g., alkyl iodide). The relatively mild conditions in which the xanthate suffers a  $\beta$ -elimination (Chugaev elimination) were used for the preparation of alkenes from alcohols. The reaction of elimination is common, although some side reactions were detected and investigated, including homolytic cleavage of the S–R bond and isomerization into dithiolcarbonate [138]. The three possible paths of thermal decomposition are shown below:

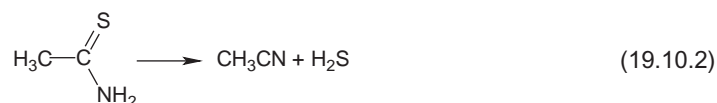




It was determined that the higher the stability of the free radical resulting from the S-substituent, the stronger was the tendency for the xanthate to suffer a homolytic cleavage [139]. The formation of dithiolcarbonates and kinetic parameters for Chugaev elimination were reported for various xanthates [140,141].

### Thioamides

Thioamides typically decompose upon heating with formation of H<sub>2</sub>S, as shown in the following reaction for thioacetamide:



Other thioamides were investigated regarding their thermal decomposition. These include thiobenzamide [142], *N*-acetylthiobenzamide [142,143], and *N*-benzoylthiobenzamide [142]. Kinetic parameters for the decomposition of *N*-acetylthiobenzamide were reported in the literature [143]. Thioamides also have the capability to form stable complexes with certain metal ions. Thermal stability of some such complexes has been reported in the literature [144].

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## CHAPTER 20

## *Pyrolysis of Derivatives of Carbonic Acid with Nitrogenous Functionalities*

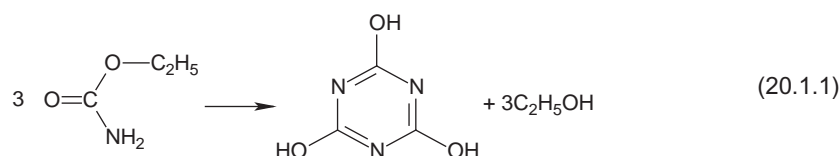
### 20.1. AMIDES OF CARBONIC ACID (CARBAMATES AND UREAS)

#### *General aspects*

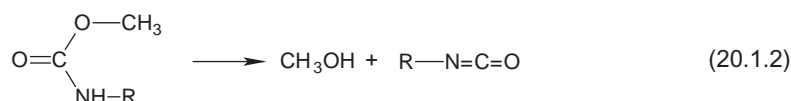
Carbonic acid  $\text{O}=\text{C}(\text{OH})_2$  is not a stable compound, being present only in small amounts in the solutions of  $\text{CO}_2$  in water. The formal replacement of one OH group in the formula of carbonic acid with  $\text{NH}_2$  leads to carbamic acid  $\text{H}_2\text{N}-\text{C}(=\text{O})-\text{OH}$ , also not known as a free compound. However, the compound resulting from the formal replacement of both OH groups with  $\text{NH}_2$  is a well-known compound, carbodiamide (urea), with the formula  $\text{H}_2\text{N}-\text{C}(=\text{O})-\text{NH}_2$ . The formal replacement of hydrogen atoms from carbamic acid and from urea with organic radicals leads to stable compounds known as carbamates (urethanes) in the case of carbamic acid, and as substituted ureas in the case of urea.

#### *Urethanes (carbamates)*

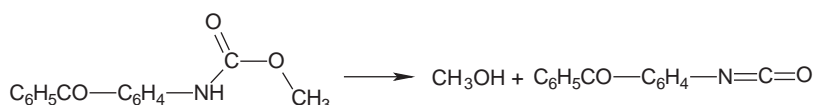
Ethyl carbamate or ethyl urethane decomposes at boiling point to generate a mixture of compounds, including cyanuric acid (trimer of cyanic acid  $\text{HNCO}$ ) by the following reaction:



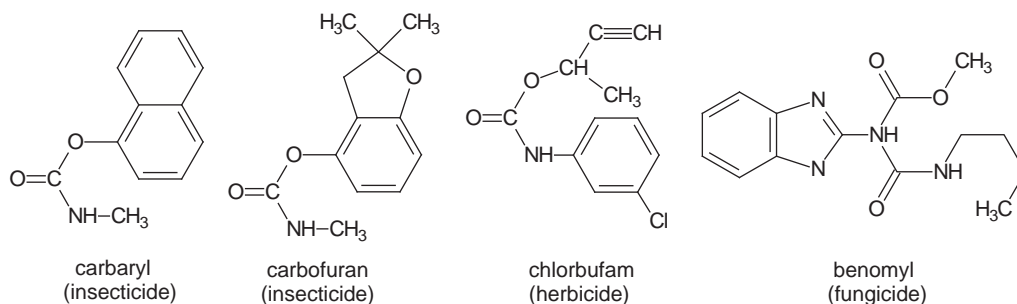
Cyanuric acid  $(\text{HNCO})_3$  is present in two tautomeric forms, 1,3,5-triazine-2,4,6-triol, and 1,3,5-triazine-2,4,6-(1H,3H,5H)-trione. A substituted urethane at the nitrogen generates by pyrolysis an isocyanate, as shown in the following reaction:



The reaction was verified, for example, for methyl *p*-benzoylphenylurethane, which generates *p*-benzoylphenyl isocyanate [1].



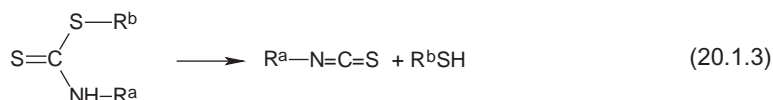
A large number of carbamates were synthesized and used as pesticides. These include insecticides, herbicides, and fungicides, four of the formulas of these compounds being shown below:



Pyrolysis of some of these pesticides is of special concern regarding the potential to generate other compounds that can be harmful to the environment, mainly when a specific compound is extensively used on crops, such as the case of carbofuran or of carbaryl (Sevin<sup>®</sup>). Pyrolysis of carbofuran, for example, performed at 750 °C generated a complex mixture containing 86 identifiable molecular fragments [2]. A large number of mono aromatics and polycyclic aromatic hydrocarbons were detected in the pyrolysate, in addition to some oxygenated heterocyclic compounds.

### Thiocarbamates

Sulfur-containing derivatives of carbamic acid are present in tautomeric forms thiol/thioketone. For example, thiocarbamic acid NH<sub>2</sub>-C(=S)-OH has also the formula NH=C(SH)OH and can give S-alkylated derivatives. S-ethyl thiocarbamate decomposes around 150 °C to generate ethyl mercaptan (equivalent to ethanol) and cyanuric acid by a reaction similar to 20.1.1. Substituted dithiourethanes decompose with the formation of mercaptans and isothiocyanates, similarly to substituted urethanes, as shown in the following reaction:



Similar to carbamates, thiocarbamates have important utilization as pesticides and in other practical applications. A group of such compounds are related to ethylene-bis-(dithiocarbamate). This compound can form complexes with some metal ions, such as Zn<sup>2+</sup> (zineb), Mn<sup>2+</sup> (maneb), and Mn<sup>2+</sup> and Zn<sup>2+</sup> (mancozeb), which have a polymeric type structure (connected by the divalent cation). The resulting pesticides are cholinesterase inhibitors and have practically no volatility. Related pesticides are nabam or disodium ethylenebis(dithiocarbamate), which is not polymeric, and metiram, which is tri-amminozinc ethylene-bis(dithiocarbamate)-poly[ethylenebis(thiuram disulfide)]. Polymeric pesticides have very low acute toxicity to mammals, although ethylenethiourea (ETU or 2-imidazolidinethione), a metabolite of these pesticides, is classified as a probable human carcinogen. The compounds are toxic to aquatic organisms. Pyrolysis of these pesticides was performed in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 800$  °C,  $\beta = 10$  °C/ms, THT = 10 s, and housing temperature  $T_{\text{hou}} = 280$  °C, followed by GC/MS analysis under conditions given in Table 4.6.2 (on a DB-5MS column). The pyrogram of mancozeb is shown in Figure 20.1.1, and the identified compounds are listed as a function of retention times in Table 20.1.1. (Note: Numbers in bold in this and in subsequent tables indicate the major pyrolysis constituents.) The pyrogram of nabam is shown in Figure 20.1.2, with the compounds listed in Table 20.1.2. The pyrogram of zineb is shown in Figure 20.1.3, with the compounds listed in Table 20.1.3, and the pyrogram of metiram is shown in Figure 20.1.4, with the compounds listed in

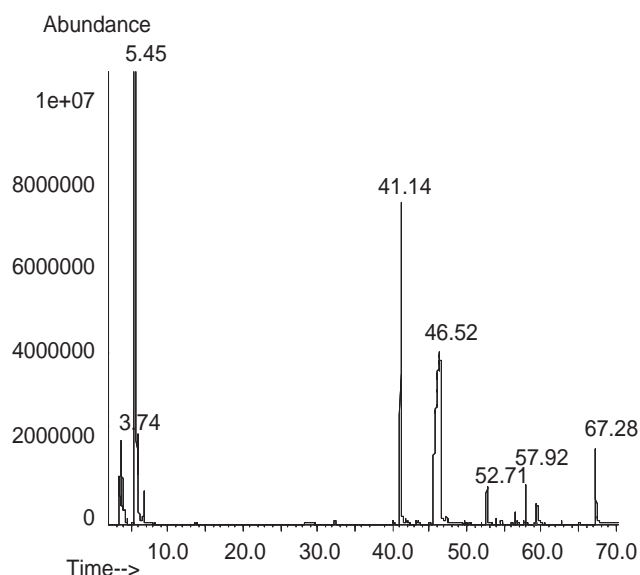


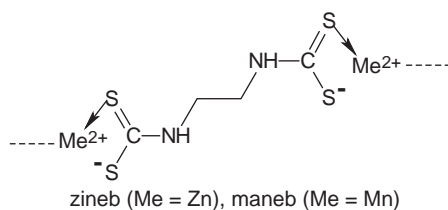
FIGURE 20.1.1. Pyrogram obtained at 800°C for mancozeb.

TABLE 20.1.1. Peak identification as a function of retention time for the pyrogram of mancozeb shown in Figure 20.1.1

No.	Compound	Ret. time (min)	MW	CAS no.	Moles (%)
1	Carbon dioxide	3.50	44	124-38-9	1.95
2	Carbonyl sulfide	3.62	60	463-58-1	0.37
3	Sulfur dioxide	3.74	64	7446-09-5	4.94
5	Carbon disulfide	5.45	76	75-15-0	<b>54.15</b>
7	Thiirane	6.70	60	420-12-2	1.36
8	Unknown	41.14	144	N/A	4.39
9	2-Imidazolidinethione (ETU)	46.52	102	96-45-7	<b>29.78</b>
11	Unknown	52.71	146	N/A	0.61
12	Unknown	56.48	202	N/A	0.12
13	Unknown	57.92	204	N/A	0.45
14	Unknown	59.25	212	N/A	0.16
15	Unknown	59.46	187	N/A	0.56
16	Unknown	67.28	216	N/A	1.15

Note: H<sub>2</sub>, H<sub>2</sub>O, HCN, CO, NH<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>, not included due to the MS settings.

Table 20.1.4. The pyrogram of maneb (not shown) was almost identical to that of mancozeb. In all pyrolysates char was generated, and together with several very low molecular weight compounds (such as H<sub>2</sub>O and HCN) was not included in mole percent calculation.



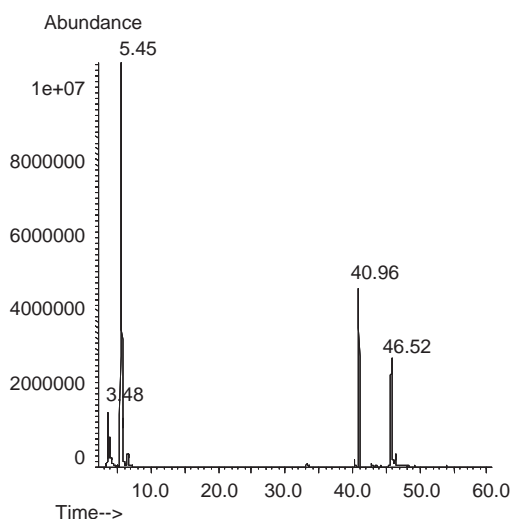


FIGURE 20.1.2. Pyrogram obtained at 800°C for nabam.

TABLE 20.1.2. Peak identification as a function of retention time for the pyrogram of nabam shown in Figure 20.1.2

No.	Compound	Ret. time (min)	MW	CAS no.	Moles (%)
1	Carbon dioxide	3.48	44	124-38-9	3.75
2	Carbonyl sulfide	3.62	60	463-58-1	0.94
3	Sulfur dioxide	3.68	64	7446-09-5	2.34
4	Nitrous oxide?	3.87	44	10024-97-2	2.52
5	Carbon disulfide	5.45	76	75-15-0	<b>67.55</b>
6	1,2,5-Trithiepane	40.96	152	6576-93-8	4.07
7	2-Imidazolidinethione (ETU)	46.52	102	96-45-7	<b>18.83</b>

Note: H<sub>2</sub>, H<sub>2</sub>O, HCN, CO, NH<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>, not included due to the MS settings.

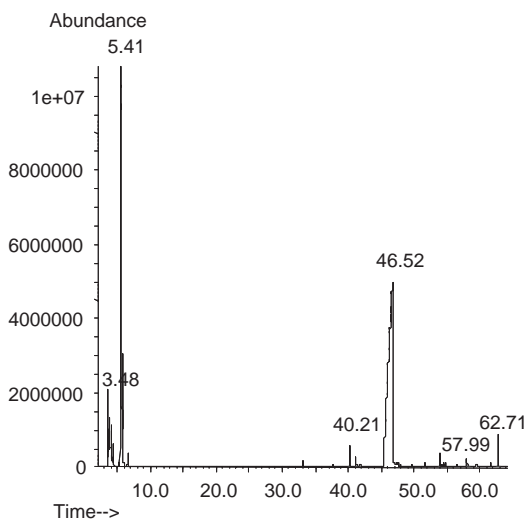


FIGURE 20.1.3. Pyrogram obtained at 800°C for zineb.



TABLE 20.1.3. Peak identification as a function of retention time for the pyrogram of zineb shown in Figure 20.1.3

No.	Compound	Ret. time (min)	MW	CAS no.	Moles (%)
1	Carbon dioxide	3.48	44	124-38-9	3.79
2	Carbonyl sulfide	3.60	60	463-58-1	2.88
3	Sulfur dioxide	3.69	64	7446-09-5	3.34
4	Methanthiol	4.44	48	74-93-1	1.35
5	Carbon disulfide	5.41	76	75-15-0	<b>38.06</b>
6	Thiirane	6.68	60	420-12-2	0.84
7	1,2,3,4-Tetrathiane	40.21	156	290-81-3	0.36
8	2-Imidazolidinethione (ETU)	46.52	102	96-45-7	<b>48.83</b>
9	Triethylenemelamine	57.99	204	51-18-3	0.22
10	1,4-Bis(2-thiazolin-2-yl)piperazine	62.71	256	N/A	0.33

Note: H<sub>2</sub>, H<sub>2</sub>O, HCN, CO, NH<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>, not included due to the MS settings.

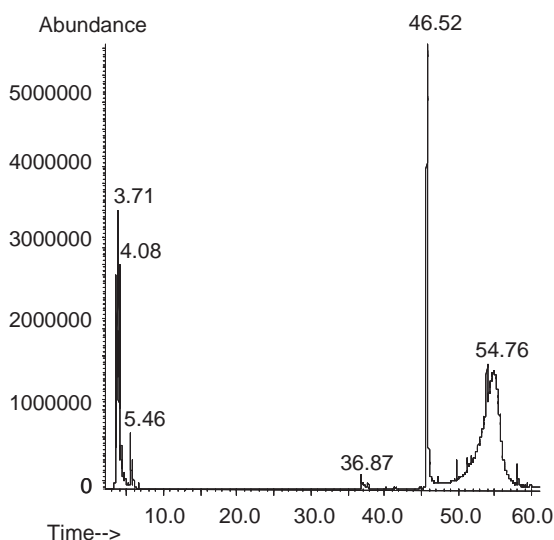
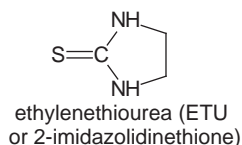


FIGURE 20.1.4. Pyrogram obtained at 800 °C for metiram.

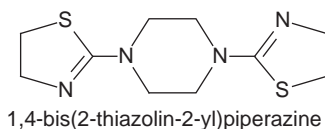
TABLE 20.1.4. Peak identification as a function of retention time for the pyrogram of metiram shown in Figure 20.1.4

No.	Compound	Ret. time (min)	MW	CAS no.	Moles (%)
1	Carbon dioxide	3.49	44	124-38-9	9.18
2	Sulfur dioxide	3.71	64	7446-09-5	<b>12.63</b>
3	Nitrous oxide?	3.90	44	10024-97-2	8.28
4	Unknown	4.08	64	N/A	6.69
5	Carbon disulfide	5.46	76	75-15-0	3.00
6	2-Imidazolidinone	36.87	86	120-93-4	1.84
7	2-Imidazolidinethione (ETU)	46.52	102	96-45-7	<b>39.94</b>
8	Sulfur (S <sub>8</sub> )	54.76	256	10544-50-0	<b>18.44</b>

Note: H<sub>2</sub>, H<sub>2</sub>O, HCN, CO, NH<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>, not included due to the MS settings.

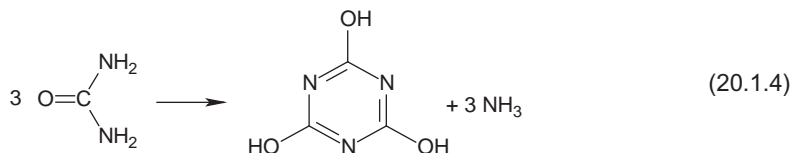


As shown in Figures 20.1.1–20.1.4 and the associated tables, the pyrograms showed some differences. Although ethylenethiourea (2-imidazolidinethione or ETU) was present in all pyrolysates, the compound was not at the same level in all pyrolysates. Also  $\text{CS}_2$  was a common decomposition product and was present at different levels in the different pyrolysates. In the mancozeb pyrolysate there were a number of peaks that were not identified. The spectra of these peaks contained mainly the molecular ion and little fragmentation, indicating stable (probably heterocyclic) molecules. The pyrograms also contained specific compounds for each pesticide such as 1,4-bis(2-thiazolin-2-yl)piperazine for zineb, 1,2,5-tritripane for nabam, and sulfur  $\text{S}_8$  for metiram.

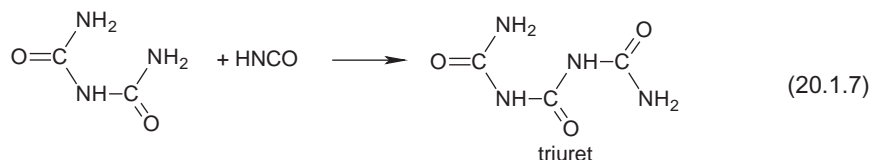
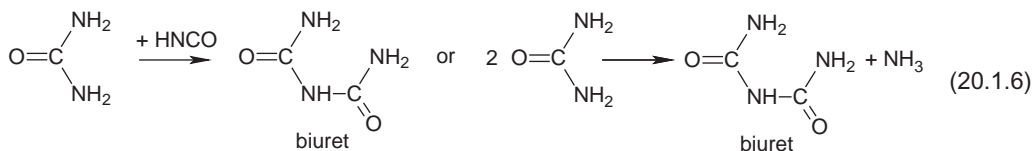
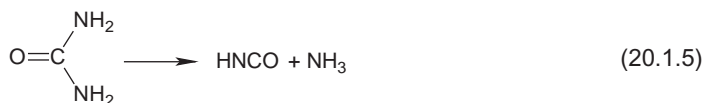


### Urea and substituted ureas

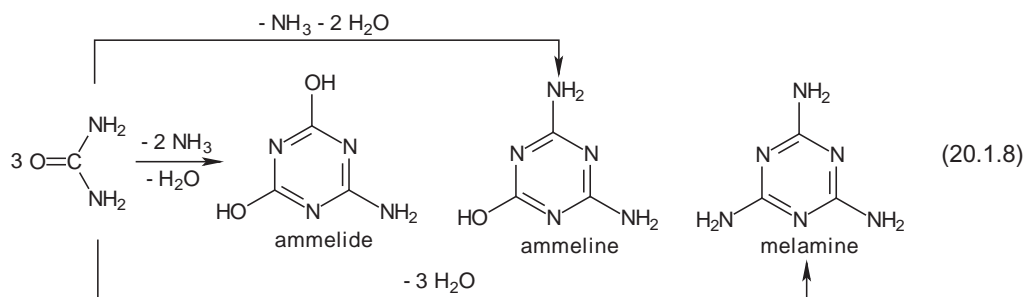
Urea was synthesized initially by thermal decomposition of ammonium isocyanate [3]. Urea itself decomposes around  $175^\circ\text{C}$  to generate ammonia and cyanuric acid, as shown in the following reaction:



However, the reaction also generates some unstable cyanic acid  $\text{HNCO}$ , as well as biuret, triuret, etc., as shown in the following reactions:

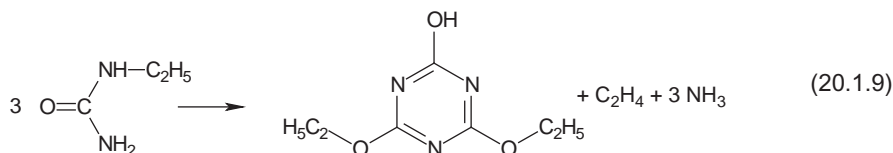


When temperature increases above  $190^\circ\text{C}$ , several cyclic compounds are formed. At  $190^\circ\text{C}$  ammelide is found in the pyrolysate; when temperatures increase to around  $225^\circ\text{C}$ , ammeline is generated; and above  $325^\circ\text{C}$  the formation of melamine is detected.



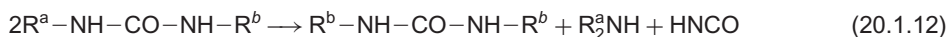
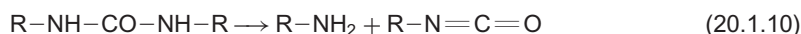
Ammelide and ammeline start to decompose above their formation temperature, and in the presence of  $\text{H}_2\text{O}$  (also produced in the reaction), they generate  $\text{NH}_3$  and  $\text{CO}_2$ .

Monoethylurea decomposes with the formation of various fragments and condensation products, including the formation of  $\text{NH}_3$  and diethylcyanurate by reactions similar to 20.1.1, as shown below [4]:

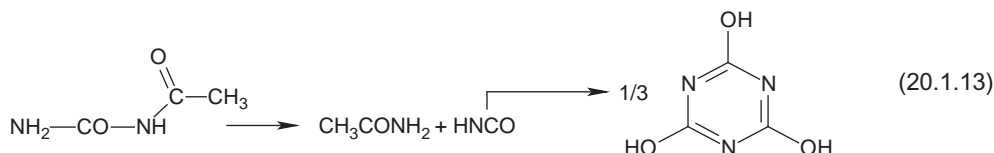


Monophenyl urea on the other hand, generates when heated for 2 h at  $160^\circ\text{C}$  diphenyl urea and urea (by a disproportionation reaction).

Disubstituted ureas can be symmetrical (one identical radical to each nitrogen) or unsymmetrical with both radicals on the same nitrogen or with different radicals on the same or on different nitrogens. The decomposition of these compounds depends on their structure and on the nature of the radical. Among the possible reactions are elimination of isocyanic acid and an amine, elimination of an isocyanate and an amine, disproportionation, etc. Some of these possible reactions are shown below:



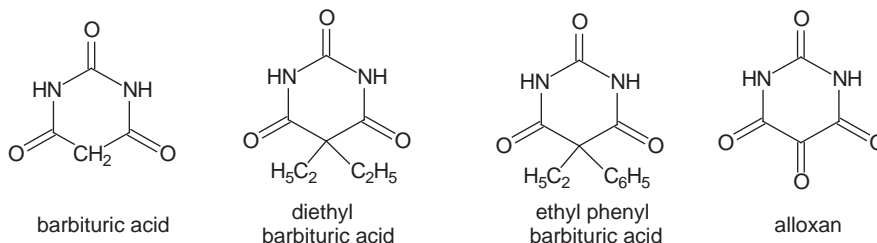
The hydrogen from the urea can be replaced by acyl groups. Pyrolysis of these compounds is similar to that of ureas substituted with alkyl or aryl. For example, acetyl urea decomposes to form cyanuric acid and acetamide by the following reaction [5]:



The kinetic parameters for Arrhenius equation of  $\text{HNCO}$  elimination from *N*-acetylurea are  $A = 7.94 \cdot 10^{+10}$  and  $E^\ddagger = 43.3 \text{ kcal/mol}$  [5]. Methyl acetyl urea in a similar reaction generates around  $180^\circ\text{C}$  methyl isocyanate and acetamide [1]. Diacetyl urea decomposes around  $170^\circ\text{C}$  to generate acetamide, diacetamide,  $\text{CO}_2$ ,  $\text{CH}_3\text{CN}$ , and cyanuric acid.

A special molecule generated from urea by alkylation with malonic acid is barbituric acid or 2,4,6-(1H,3H,5H)pyrimidinetrione. Similarly to Meldrum's acid, barbituric acid has two acidic hydrogen atoms

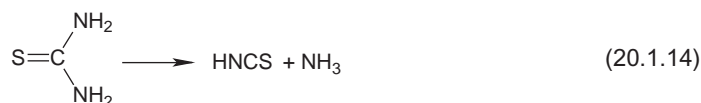
that can be replaced with various substituents, for example in Knoevenagel type condensation reactions. A related compound to barbituric acid is alloxan. The formulas of barbituric acid, diethylbarbituric acid (Veronal), phenyl ethyl barbituric acid (phenobarbital), and alloxan are shown below:



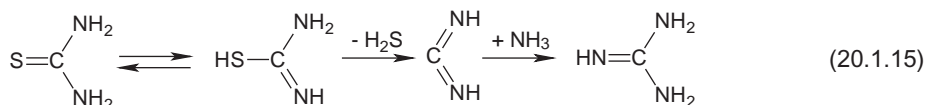
Barbituric acid is stable up to about 250 °C. Its decomposition takes place with the elimination of water and formation of various fragments by the scission of the ring including the formation of amines. Thermal decomposition of the other compounds starts at even lower temperatures. Around 170 °C the decomposition can take place in the initial phase by the loss of the substituent, followed by ring scissions [6].

### Thiourea

Thiourea can be synthesized in a reaction similar to that for urea, by thermal decomposition of ammonium thiocyanate. Upon heating the main reaction of thiourea decomposition around 170 °C is the formation of thiocyanic acid and ammonia in a reaction similar to 20.1.2, as shown below:

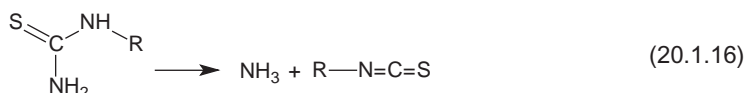


Thiourea has a higher tendency compared to urea to be in equilibrium with isothiurea and to generate guanidine when heated for extensive periods of time (20 h) at 190 °C. The sequence of possible reactions in this process is shown below:



The necessary NH<sub>3</sub> for reaction 20.1.15 is generated by the parallel reaction 20.1.14. Substituted thioureas also were evaluated regarding their behavior upon heating [1]. The substitution in the thiourea molecule can be done with alkyl, aryl, or acyl radicals. Also, since thiourea can be present as isothiurea, S-alkyl thioureas are known.

Pyrolysis of alkyl thioureas typically takes place with the formation of isothiocyanates, as shown in the following reaction:



An example of a substituted thiourea pyrolysis is given below for 1-ethyl-2-thiourea. The material was pyrolyzed in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 800$  °C,  $\beta = 10$  °C/ms, THT = 10 s, and housing temperature  $T_{\text{hou}} = 280$  °C. From 1.0 mg 1-ethyl-2-thiourea the pyrogram from Figure 20.1.5 was generated when the analysis of the pyrolysate was done by GC/MS under

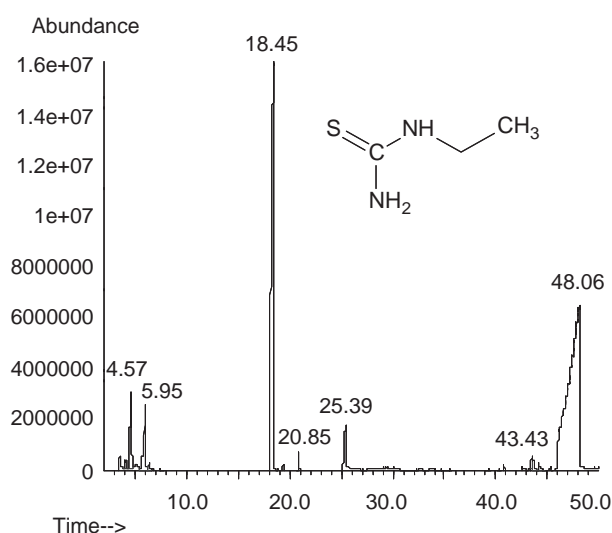


FIGURE 20.1.5. Pyrogram obtained at 800 °C for 1-ethyl-2-thiourea (MW = 104).

TABLE 20.1.5. Peak identification as a function of retention time for the pyrogram of 1-ethyl-2-thiourea shown in Figure 20.1.5

No.	Compound	Ret. time (min)	MW	CAS no.	Moles (%)
1	Carbon dioxide	3.52	44	124-38-9	0.59
2	Ethylamine	4.58	45	75-04-7	<b>9.34</b>
3	Carbon disulfide	5.95	76	75-15-0	3.61
4	Ethane isocyanate	6.37	71	109-90-0	0.36
5	Ethane isothiocyanate	18.45	87	542-85-8	<b>34.42</b>
6	Diethylcyanamide	19.37	98	617-83-4	0.09
7	4,5-Dihydro-4,5-dimethyl-1H-pyrazole	20.85	98	28019-94-5	0.53
8	Methyl vinyl ketone	25.39	70	78-94-4	3.52
9	<i>N,N'</i> -Diethylthiourea	43.43	132	105-55-5	0.17
10	<i>N,N'</i> -Diethylthiourea?	43.58	132	N/A	0.37
11	2-Imidazolidinethione (ETU)	48.06	102	96-45-7	<b>47.01</b>

Note: H<sub>2</sub>, H<sub>2</sub>O, HCN, CO, NH<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>, not included due to the MS settings.

conditions given in Table 4.6.2 (DB-5MS column). The peak identification from the pyrogram is given in Table 20.1.5.

As shown in Table 20.1.5, the main pyrolysis products of 1-ethyl-2-thiourea are ethane isothiocyanate (as expected) and also the heterocycle 2-imidazolidinethione. The elevated temperature where the pyrolysis was performed explains the formation of a stable heterocyclic compound.

The presence in the pyrolysate of low levels of oxygenated compounds such as CO<sub>2</sub>, ethane isocyanate, and methyl vinyl ketone can be explained either by the presence of traces of air during pyrolysis, the presence of water, or an impurity in the 1-ethyl-2-thiourea used as a sample. The formation of ethylene thiourea (ETU) is very likely influenced by the high thermal stability of the ETU cycle.

2-Ethylenethiourea also decomposes when pyrolyzed at high temperatures. In Figure 20.1.6 is shown a pyrogram obtained starting with 0.2 mg ETU. The results were obtained from a Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 800$  °C,  $\beta = 10$  °C/ms, THT = 10 s, and housing temperature  $T_{hou} = 280$  °C and with the analysis done by GC/MS under conditions given in Table 4.6.2 (DB-5MS column). Peak identification is given in Table 20.1.6.

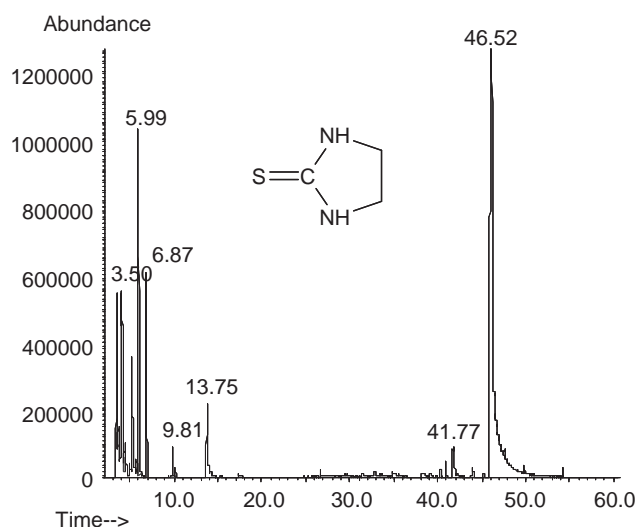


FIGURE 20.1.6. Pyrogram obtained at 800 °C for 2-ethylenethiourea (ETU) ( $MW = 102$ ).

TABLE 20.1.6. Peak identification as a function of retention time for the pyrogram of 2-ethylenethiourea (ETU) shown in Figure 20.1.6

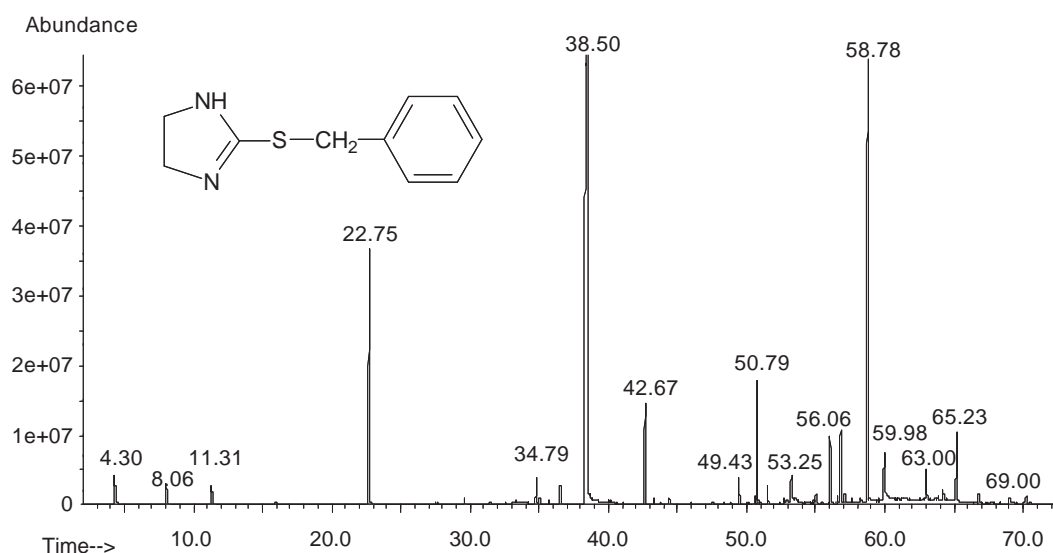
No.	Compound	Ret. time (min)	MW	CAS no.	Moles (%)
1	Carbon dioxide	3.50	44	124-38-9	<b>11.61</b>
2	Carbonyl sulfide	3.69	60	463-58-1	3.46
3	Sulfur dioxide	3.71	64	7446-09-5	<b>7.98</b>
4	Methyl isocyanide	5.25	41	593-75-9	<b>10.71</b>
5	Carbon disulfide	5.99	76	75-15-0	<b>9.33</b>
6	Thiirane	6.87	60	420-12-2	<b>7.29</b>
7	Benzene	9.81	78	71-43-2	0.94
8	Isothiazole	13.75	85	288-16-4	3.10
9	Unknown	41.77	144	N/A	1.43
10	2-Imidazolidinethione (ETU not decomposed)	46.52	102	96-45-7	<b>44.14</b>

Note:  $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$ , not included due to the MS settings.

Phenylthiourea starts decomposing around 160 °C with the formation of aniline and HNCS. A parallel reaction leads to the formation of  $NH_3$  and phenylisothiocyanate.

S-Methyl-thiourea decomposition at low temperatures (80 °C) generates methylthiol and cyanuric acid. An S-substituted 2-imidazolidinethione, namely 2-(phenylmethyl-thio)-2-imidazoline or S-benzyl-2-ethylenethiourea, was selected to determine its pyrolysis products at 900 °C. The pyrolysis was performed in a Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900$  °C,  $\beta = 10$  °C/ms, THT = 10 s, and housing temperature  $T_{hou} = 280$  °C, followed by GC/MS analysis under conditions given in Table 4.6.1 (on a DB-1701 column). The pyrogram is given in Figure 20.1.7. Peak identification is given in Table 20.1.7.

At decomposition temperatures of 900 °C for S-benzyl-2-ethylenethiourea, the main reaction is the cleavage of the bonds connecting the imidazoline group with the sulfur atom and the bond connecting the sulfur atom with the benzyl group, generating fragments such as toluene, benzyl sulfide, and benzene-methanethiol. Few fragments containing imidazoline or 1H-imidazole were detected in the pyrolysate.

FIGURE 20.1.7. Pyrogram obtained at 900°C for *S*-benzyl-2-ethylenethiourea.TABLE 20.1.7. Peak identification as a function of retention time for the pyrogram of *S*-benzyl-2-ethylenethiourea shown in Figure 20.1.7

No.	Compound	Ret. time (min)	MW	CAS no.	Moles (%)
1	Hydrogen sulfide	4.30	34	7783-06-4	<b>5.40</b>
2	Carbon disulfide	8.06	76	75-15-0	1.33
3	Thiirane	11.31	60	420-12-2	2.01
4	Toluene	22.75	92	108-88-3	<b>16.69</b>
5	Styrene	29.62	104	100-42-5	0.17
6	Benzaldehyde	34.79	106	100-52-7	0.78
7	Benzonitrile	36.55	103	100-47-0	0.55
8	Benzenemethanethiol	38.50	124	100-53-8	<b>44.94</b>
9	Benzyl nitrile (benzyl cyanide)	42.67	117	140-29-4	2.61
10	1H-Pyrrole carboxaldehyde?	44.43	95	1003-29-8	0.28
11	1,3-Dimethylimidazole-2(3H)-thione?	49.43	128	6596-81-2	1.20
12	Bibenzyl	50.79	182	103-29-7	1.98
13	Unknown	51.56	163	N/A	0.32
14	2-Phenylthiazolidine	52.71	165	4569-82-8	0.22
15	4,5-Dihydro-2-phenyl-1H-imidazole	53.25	146	936-49-2	0.89
16	1-(Phenylmethyl)-1H-imidazole	55.03	158	4238-71-5	0.24
17	Stilbene	56.06	180	588-59-0	1.07
18	<i>N</i> -Benzylidenebenzylamine	56.82	195	780-25-6	1.07
19	1-(2-Aminophenyl)pyrrole	57.11	158	6025-60-1	0.22
20	Benzyl sulfide	58.78	214	538-74-9	<b>11.80</b>
21	2-Imidazolidinethione (ETU)	59.98	102	96-45-7	3.29
22	9-Cyano-9,10-dihydrophenanthrene?	63.00	205	56666-55-8	0.73

(Continued)

TABLE 20.1.7. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Moles (%)
23	<i>N,N</i> -Dibenzylideneethylenediamine (1 <i>E</i> ,5 <i>E</i> ), (1 <i>E</i> ,5 <i>E</i> )-2,5-diaza-1,6-diphenylhexa-1,5-diene	64.23	236	104-71-2	0.17
24	Bis-(phenylmethyl)disulfide	65.23	246	150-60-7	1.39
25	Unknown	66.78	202	N/A	0.26
26	Unknown	69.00	204	N/A	0.19
27	<i>N,N</i> -Dibenzylideneethylenediamine (1?,5?)	70.24	236	N/A	0.20

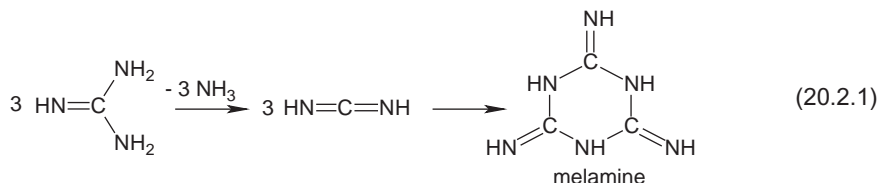
Notes: H<sub>2</sub>, H<sub>2</sub>O, HCN, CO, NH<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>, not included due to the MS settings.  
 “?” indicates tentative compound or tentative isomer position.

*N*-Acetylthiourea and *N,N*-diacetylthiourea eliminate HNCS similar to acylureas. Some kinetic parameters for these decompositions are reported in the literature [5].

## 20.2. GUANIDINE AND RELATED COMPOUNDS

### General aspects

By replacing the =O with =NH in urea, a compound with the formula HN=C(NH<sub>2</sub>)<sub>2</sub>, known as guanidine, is generated. Some important amino acids such as arginine and creatine are derivatives of guanidine. The hydrogens in guanidine molecule can be replaced with alkyl, aryl, or acyl radicals generating substituted guanidines. Guanidine thermal decomposition leads to the formation of NH<sub>3</sub> and melamine, in a reaction as shown below [7,8]:



Guanidine has a strong basic character ( $pK_a = 12.5$ ) and forms salts with acids. Guanidine hydrochloride upon heating around 185 °C generates a compound analogous to biuret.

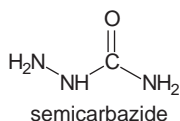
Triphenyl guanidine  $\text{C}_6\text{H}_5\text{N}=\text{C}(\text{NHC}_6\text{H}_5)_2$  generates by thermal decomposition aniline and carbodiphenylimide  $\text{C}_6\text{H}_5\text{N}=\text{C}=\text{NC}_6\text{H}_5$  [1].

## 20.3. HYDRAZIDES OF CARBONIC ACID

### General aspects

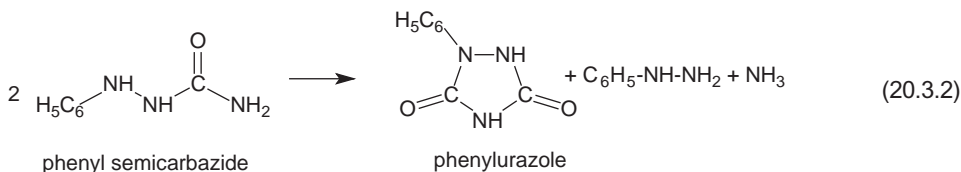
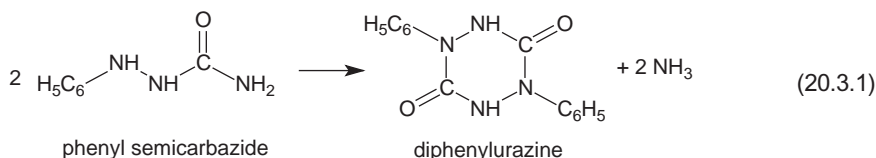
The replacement of an –OH in the formula of carbonic acid with –NH<sub>2</sub> and of the other –OH with –NH–NH<sub>2</sub> leads to semicarbazide, and the replacement of both –OH groups in the formula with –NH–NH<sub>2</sub> generates carbazide. The hydrogens from the hydrazine or amine moiety can be further replaced with organic radicals, either alkyl, aryl, or acyl.

These replacements lead to a series of compounds known as semicarbazides (from semicarbazide) or carbazides (from carbazide). Thermal decomposition of these molecules typically takes place at temperatures between 150 °C and 250 °C and the composition of the resulting product depends on the complexity of the parent molecule. For example, thermal decomposition of phenyl semicarbazide

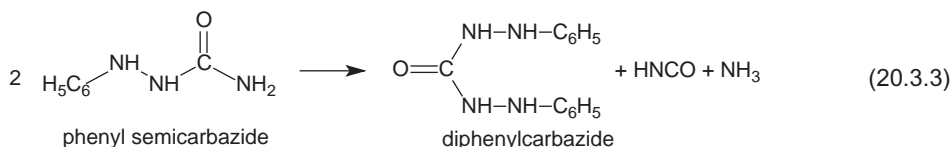




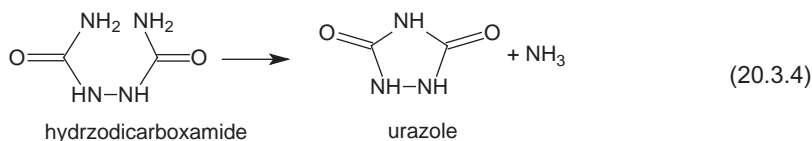
around 170 °C takes place with the formation of diphenylurazine and phenylurazole as shown in the following reactions [1]:



The stability of the heterocyclic compounds is probably the main reason for their formation in semicarbazide pyrolysate. It is possible that an intermediate reaction with the formation of diphenylcarbazine takes place before the formation of final products, but diphenylcarbazine is further decomposed to generate diphenylurazine and phenylurazole. The reaction of formation of diphenylcarbazine is shown below:



Similarly to reaction 20.3.2, hydrazodicarboxamide generates urazole by pyrolysis around 200 °C:



The hydrogen atoms from semicarbazide or carbazide can be replaced by acyl groups. Also, the hydrazine moiety can react with carbonyl compounds. The oxygen atom in the formulas of semicarbazide or carbazide can be replaced with sulfur to generate thiosemicarbazide or thiocarbazide, respectively. Some studies regarding thermal decomposition of these compounds are available in the literature [1].

## 20.4. NITRILES OF CARBONIC ACID (CYANATES AND ISOCYANATES)

### General aspects

The replacement with -CN of the -COOH group from the formula of carbonic acid written HO-COOH generates cyanic acid HOCN. A series of compounds known as cyanates can be generated by the replacement of the hydrogen atom in HOCN with organic radicals. An isomer of cyanic acid is isocyanic acid HNCO, and this compound also generates a series of organic compounds known as isocyanates. Cyanic acid easily forms trimers (cyanuric acid) or higher oligomers such as pentacyanic acid. These compounds decompose by heating at temperatures around 350 °C to form the monomer. The same tendency to polymerize is characteristic for alkyl cyanates. These compounds decompose either with

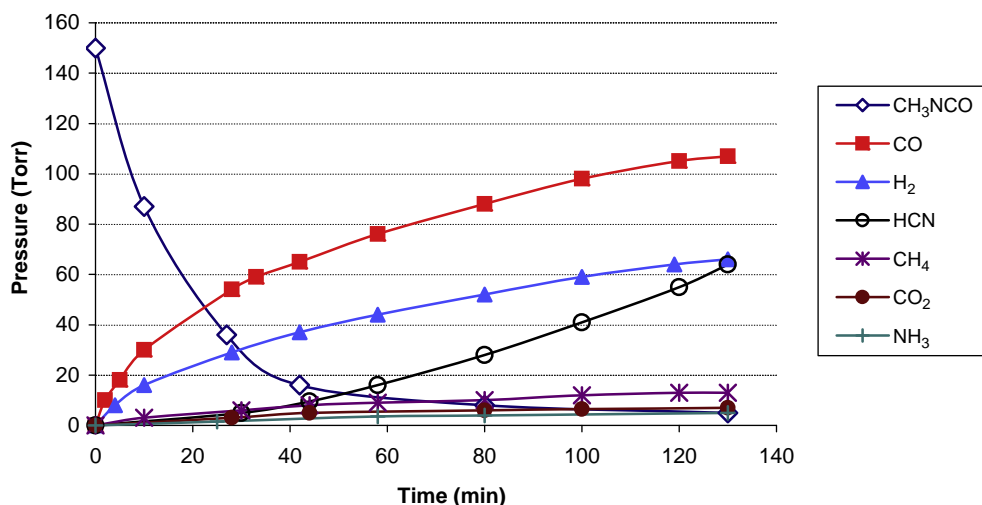


FIGURE 20.4.1. Variation with heating time in partial pressures of different reaction products of methyl isocyanate at 526°C and 150 Torr for the initial material [10].

the generation of the monomer or decompose with the formation of cyanic acid and alkenes. For example, triethylcyanurate decomposes with the formation of cyanic acid and C<sub>2</sub>H<sub>4</sub> [9].

Isocyanates are compounds with the general formula R–N=C=O. Methyl isocyanate thermal decomposition has been investigated in the temperature range 427–548°C at pressure between 55 and 300 Torr, in a static reaction vessel [10]. The main decomposition reaction is the following:



The mechanism of this reaction is radicalic, and has the order 1.5 with the Arrhenius equation  $\log k$  ( $\text{L}^{1/2}/\text{mol}^{1/2}/\text{s}$ ) =  $13.12 \pm 0.06 - (56,450 \pm 1670 \text{ cal/mol})/2.303 RT$ . The graphs showing the variation with heating time of the partial pressures of different reaction products of methyl isocyanate starting at 526°C and 150 Torr for the initial material is shown in Figure 20.4.1 [10].

Other isocyanates behave similarly to cyanates. For example, phenyl isocyanate dimer changes into phenyl isocyanate when heated above 175°C.

## 20.5. REFERENCES

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## CHAPTER 21

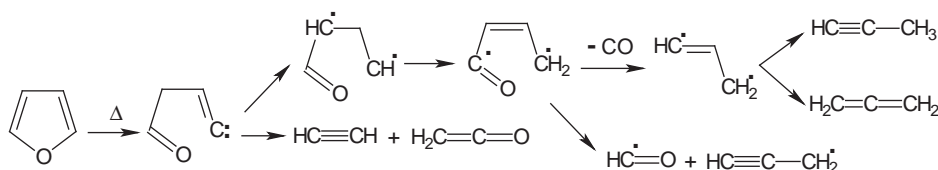
*Pyrolysis of Aromatic Heterocyclic Compounds***21.1. AROMATIC HETEROCYCLES CONTAINING OXYGEN*****General aspects***

Heterocyclic compounds are organic compounds with a ring structure that contains in the cycle at least one carbon atom and one other element, such as N, O, or S. The most common cycles contain five or six atoms, the stability of these rings being higher than that of three, four, seven, or larger rings. However, many heterocyclic compounds with a different number of atoms larger than five or six are known. Heterocyclic rings are either nonaromatic or aromatic. Most nonaromatic heterocyclic compounds are similar in their chemical properties with acyclic compounds. Examples include cyclic ethers, which are similar to ethers, cyclic secondary amines, which are similar to linear secondary amines, etc. These compounds were discussed in previous chapters. Also other cycles containing heteroatoms such as carbohydrates (in cyclic form), lactones, anhydrides, etc., which do not have an aromatic character, were previously discussed. In the present section, the pyrolysis of oxygen-containing cycles with aromatic character, including compounds related to furan and pyrylium ion, will be presented. Heterocyclic compounds may contain a single cycle or more cycles, which can be isolated or condensed. Compounds with carbon aromatic cycles condensed with heterocycles are also common. Polycyclic aromatic compounds containing heterocycles are sometimes indicated as hetarenes (PHAs).

***Furan and furan-related compounds***

Furan is an aromatic compound with the participation of the oxygen lone pair in the  $\pi$  electron system to satisfy Hückel's rule,  $4n+2$  ( $n = 1$ ) electrons. The compound is stable to heating up to about 550 °C (also depending on heating time). Furan pyrolysis was reported in the literature for continuous flow pyrolysis that generated mainly water, methane, ethylene, acetylene, and benzene [1]. In a shock wave experiment in the temperature range 1050–1460 K, propyne, carbon monoxide, acetylene, and, indirectly, ketene were identified as main products. At high temperatures, allene, 1,3-butadiene, ethylene, methane, 1,3-butadiyne, and benzene were found as secondary products [2]. Further studies [3] were able to identify ketene directly. At low-pressure pyrolysis, only acetylene, ketene, propyne, and CO were identified as products in the pyrolysis [4].

Pyrolysis of furan was also reported in the literature for a continuous flow pyrolysis system working at atmospheric pressure with a residence time of about 20 s in a current of argon with a flow rate of 60 cm<sup>3</sup>/min and the ratio furan vapors/argon of about 1.5/1 [5]. The thermal decomposition of furan is initiated by homolytic cleavage of a C–O bond. The resulting diradical can either isomerize to a carbene or fragment in two ways, generating acetylene and ketene or free radicals, as shown in the following reactions:



Under continuous flow pyrolysis conditions, the oxygen-containing fragments CO, CHO<sup>•</sup>, and ketene were shown to have no tendency to form larger compounds in secondary reactions. However,

the not-oxygenated free radicals and molecular fragments have a high tendency to react further and generate polycyclic aromatic hydrocarbons. Various paths of generating aromatic hydrocarbons from acetylene were discussed in Section 7.6, and other similar paths can be easily suggested starting with propyne and the free radical  $C_3H_3^{\cdot}$ . The proportions of various PAHs detected in furan pyrolysis in continuous flow pyrolysis at 800 and 900 °C [5] are shown in Table 21.1.1.

The formation of PAHs and PHAs was also evaluated for benzo[*b*]furan and for dibenzofuran [5]. The results regarding the proportion of these aromatic compounds in pyrolysates of benzo[*b*]furan and dibenzofuran in a continuous flow pyrolysis experiment at 900 °C are also given in Table 21.1.1. Other data regarding the pyrolysis of these two compounds are available in the literature [6]. The formation of polycyclic aromatic hydrocarbons from furan (and derivatives) is of considerable concern, since furan itself is generated by pyrolysis of cellulosic materials (especially pine wood). Formation of PAHs in forest fires can be attributed in part to a route involving furan formation.

Kinetic parameters regarding furan pyrolysis were also reported in the literature for the unimolecular decomposition in the temperature range 1050–1270 K at very low pressure [7,3]. The process was also evaluated with ab initio quantum chemical techniques [3].

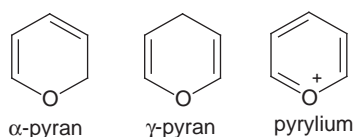
TABLE 21.1.1. Proportion of PAHs and PHAs generated in a continuous flow pyrolysis experiment for furan, benzo[*b*]furan, and for dibenzofuran [5]

Compound	Furan 800 °C (%)	Furan 900 °C (%)	Benzo[ <i>b</i> ]furan 900 °C	Dibenzofuran 900 °C
Acenaphthene	0.5	0.5	—	—
Acenaphthylene	5.9	6.4	1.1	0.3
Anthracene	3.7	2.7	6.0	0.4
Benzene	—	2.0	12.1	1.3
Benzo[1,2- <i>b</i> :4,5- <i>b'</i> ]bis[1]benzofuran	—	—	—	0.9
Benzo[ <i>a</i> ]pyrene	6.5	7.5	10.4	0.6
Benzo[ <i>b</i> ]furan	—	—	11.7	—
Benzo[ <i>b</i> ]naphtho[2,3- <i>d</i> ]furan	—	—	—	0.5
Benzo[ <i>c</i> ]phenanthrene	0.6	—	—	—
Benzo[ <i>ghi</i> ]fluoranthene.	<0.1	0.6	—	—
Biphenyl	4.1	3.7	10.5	1.1
Dibenzo[ <i>def:mno</i> ]chrysene	<0.1	1.7	—	—
Dibenzofuran	—	—	0.6	74.1
1,2'-Dinaphthalene	<0.1	—	<0.1	—
Ethenylantracene	1.1	0.8	—	—
1-Ethenylnaphthalene	1.2	0.6	—	—
Fluoranthene	6.1	9.2	5.3	3.0
Fluorine	3.1	1.6	2.8	1.1
2-Hydroxybiphenyl	—	—	—	0.7
Indene	2.8	1.0	—	0.4
2-Methylnaphthalene	3.5	0.9	—	—
Naphthalene	30.4	28.1	6.9	5.8
Phenanthrene	11.8	13.3	25.0	1.5
4-Phenyldibenzofuran	—	—	—	4.1
2-Phenylnaphthalene	2.8	2.3	0.9	0.3
Pyrene	9.9	9.8	2.4	0.6
Styrene	1.9	0.6	—	—
Triphenylene	5.6	9.1	4.1	3.0
Triphenylenofuran	—	—	—	<0.1

Pyrolysis of compounds with various functionalities attached to a furan ring shows similar thermal stability with other similar aromatic compounds. For example, furancarboxylic acid decomposes by decarboxylation similarly to benzoic acid (see reaction 17.4.20). The high stability of dibenzofuran and its formation by pyrolysis from other molecules can be related to the formation of chlorinated dibenzofurans when active chlorine atoms are formed in the same process. Studies on furan-related compounds were reported regarding oxidative pyrolysis [8], pyrolysis of substituted furans [9], etc.

### Pyran-related compounds

The six-atom cycle including one oxygen is named  $\alpha$ -pyran or  $\gamma$ -pyran, depending on the position of the oxygen atom in the cycle. These molecules do not satisfy the rule of aromaticity ( $2n+4$   $\pi$  electrons) and are not known as stable compounds. On the other hand, pyrylium salts generated by the elimination of a hydrogen atom and two electrons have a system of six  $\pi$  electrons and an aromatic type structure. A number of classes of natural compounds are pyran-related compounds.



Anthocyanins, an important class of natural compounds, are related to pyrylium salts. They are responsible for the red and blue colors of berries, cherries, red cabbage, grapes (and red wine), etc., and have antioxidant properties. Anthocyanins are glycosides of anthocyanidins. Anthocyanidins are salts of 2-phenylbenzopyrylium that have various hydroxy or methoxy substituents. The sugar in anthocyanins is usually glucose, but it can be rutinose or sophorose. In some anthocyanins, a *p*-hydroxycinnamic acid ester is also esterified with the sugar (such as in violanin and monardein). The specific substituents  $R^a$ ,  $R^b$ , ...,  $R^f$  for several anthocyanidins and anthocyanins are given in Table 21.1.2.

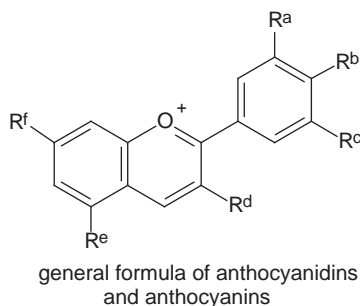


TABLE 21.1.2. Substituents in some anthocyanidins and anthocyanins

Compound	$R^a$	$R^b$	$R^c$	$R^d$	$R^e$	$R^f$
Pelargonidin	H	OH	H	OH	OH	OH
Pelargonin	H	OH	H	O-Glucose	O-Glucose	OH
Cyanidin	OH	OH	H	OH	OH	OH
Cyanin	OH	OH	H	O-Glucose	O-Glucose	OH
Malvidin	OCH <sub>3</sub>	OH	OCH <sub>3</sub>	OH	OH	OH
Malvin	OCH <sub>3</sub>	OH	OCH <sub>3</sub>	O-Glucose	O-Glucose	OH
Hirsuridin	OCH <sub>3</sub>	OH	OCH <sub>3</sub>	OH	OH	OCH <sub>3</sub>
Peonin	OCH <sub>3</sub>	OH	H	O-Glucose	O-Glucose	OH
Delphinidin	OH	OH	OH	OH	OH	OH
Petunidin	OH	OH	OCH <sub>3</sub>	OH	OH	OH

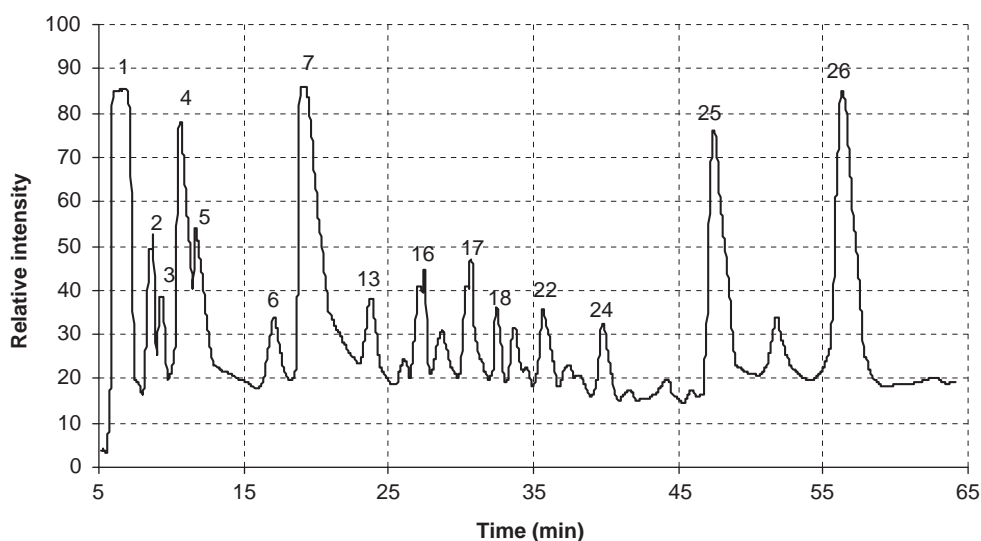


FIGURE 21.1.1. Pyrogram of cyanin [11].

TABLE 21.1.3. List of peaks identified in the pyrogram of cyanin

Peak No.	Compound	Peak No.	Compound
1	Mixture of low molecular weight compounds	14	Methylfuraldehyde
2	Acetone	15	Methylbenzoate
3	2-Methylfuran	16	Naphthalene
4	Methanol	17	<i>n</i> -Paraffn
5	Benzene	18	<i>n</i> -Paraffin
6	Toluene	19	<i>n</i> -Paraffin
7	Water	20	Guaiacol
8	Unknown	21	Dimethoxybenzene
9	Ethylbenzene	22	Phenol
10	Styrene	23	<i>o</i> -Cresol
11	2-Furaldehyde	24	<i>n</i> -Paraffin
12	Benzofuran-furylmethylketone	25	Phthalate (impurity)
13	<i>n</i> -Paraffin	26	Phthalate (impurity)

Note: Not all peaks from Table 21.1.3 are labeled on the pyrogram.

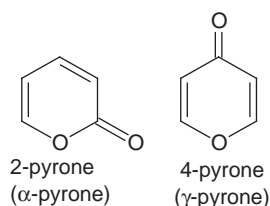
Several studies were performed on pyrolysis of anthocyanins particularly for analytical purposes [10–12]. Both the sugar moiety (glucose, rutinose, sophorose) and 2-phenylbenzopyrylium generate for some anthocyanins characteristic compounds in the pyrolysates. The aglycon generates flavone-related compounds and dihydroxy and trihydroxybenzenes [13,14]. An example of a pyrogram for cyanin is given in Figure 21.1.1. The pyrolysate was obtained in a filament pyrolyzer, and the separation of the pyrolysate components was done on a Carbowax column with the oven temperature between 30 °C and 200 °C [11]. The compounds identified in the pyrogram of cyanin are listed in Table 21.1.3.

Some characteristic fragment molecules were noticed in the pyrograms of different anthocyanidins and anthocyanins. A list of these fragment molecules for some anthocyanidins and anthocyanins is given in Table 21.1.4 [10].

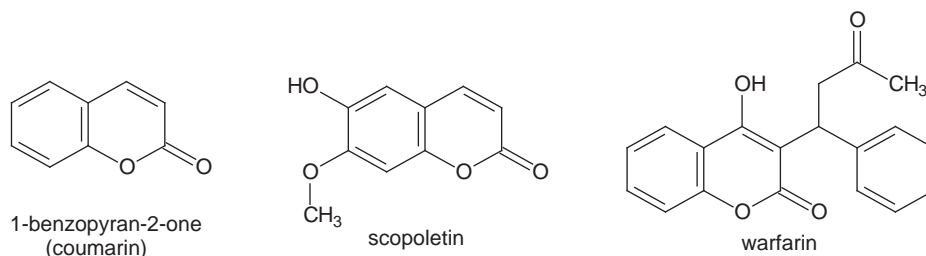
TABLE 21.1.4. Characteristic molecular fragments in the pyrolysates of some anthocyanidins and anthocyanins [10]

No.	Compound	Characteristic fragment
1	Pelargonidin	Phenol
2	Hirsutidin	2,6-Dimethoxyphenol
3	Pelargonin	Phenol
4	Cyanin	Catechol
5	Peonin	2-Methoxyphenol
6	Malvin	2,6-Dimethoxyphenol
7	Althaein	1,2,3-Trihydroxybenzene, 2,6-dimethoxyphenol, and 6-methoxycatechol
8	Myrtillin	1,2,3-Trihydroxybenzene, 2,6-dimethoxyphenol, and 6-methoxycatechol
9	Violanin	1,2,3-Trihydroxybenzene and 4-vinylphenol
10	Monardein	Phenol and 4-vinylphenol

Another group of stable compounds related to pyran structure are 2-pyrone, 4-pyrone, and their related compounds. 2-Pyrone and 4-pyrone are typically represented by a six-atom cycle containing two double bonds and a C=O group. This structure does not represent well the chemical and physical properties of the two compounds, which do not show the high unsaturation characteristic for a diene and in some reactions do not behave like ketones for 4-pyrone (e.g., do not react with hydroxylamine or phenylhydrazine) or a lactone for 2-pyrone. Pyrones have in part an aromatic character that can be assumed as coming from resonance of ketone structure with a structure containing charges on the two oxygen atoms such that six  $\pi$  electrons are present in the cycle.

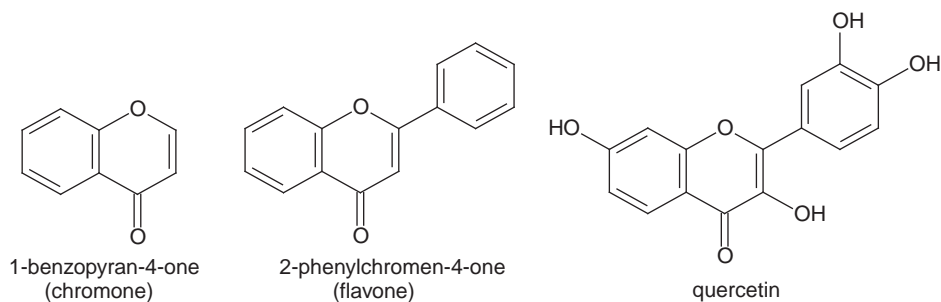


A number of natural products contain in their molecule the pyrone moiety. For example, a common naturally occurring  $\gamma$ -pyrone is 3-hydroxy-2-methyl-4H-pyran-4-one (maltol). Other compounds from this class are related to either 1-benzopyran-2-one (coumarin) or 1-benzopyran-4-one (chromone). Coumarin itself is found as a toxin in some plants. Other natural compounds related to coumarin include scopoletin, umbelliferone, and bergaptole. Warfarin, a synthetic anticoagulant, is also a derivative of 1-benzopyran-2-one. The formulas for coumarin, scopoletin, and warfarin are indicated below:



Other natural compounds have in their molecule a  $\gamma$ -pyrone moiety and are related to chromone or 2-phenylchromen-4-one (flavone). Flavones, in particular, are very common in plants, either in free form (quercetin, luteolin, morin, tangeritin, etc.) or as glycosides (rutin, quercitrin, etc.). The formulas of

chromone, flavone, and quercetin are indicated below:



Some natural compounds have a dihydrobenzopyran moiety, such as naringin and hesperidin. Pyrolysis of scopoletin is taken as an example regarding the behavior of these compounds at elevated temperatures. For this purpose, 1.0 mg scopoletin was pyrolyzed in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ . The analysis of pyrolysate was done exclusively by GC/MS under conditions given in Table 4.6.1. The time window between 45 min and 75 min from the pyrogram generated for scopoletin is shown in Figure 21.1.2. Very few compounds eluted before 45 min. Peak identification for the whole pyrogram is given in Table 21.1.5.

As shown in Table 21.1.5, scopoletin is rather stable to heating. A large proportion of the parent compound survives the flash pyrolysis, part of the compound probably evaporating before the pyrolyzer attains the  $T_{\text{eq}}$ . The decomposition takes place by the cleavage of bonds such as those with the methoxy group or C–O bonds within the pyrone ring.

A typical flavone-type compound is quercetin or to 2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4H-chromen-4-one. Quercetin is the aglycon in several glycosides such as rutin (see Section 16.3) and quercitrin. Pyrolysis of 0.9 mg quercetin was performed in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{\text{hou}} = 280^\circ\text{C}$ . The analysis of pyrolysate was done exclusively by GC/MS under conditions given in Table 4.6.1 and generated the pyrogram shown in Figure 21.1.3. Peak identification for the pyrogram is given in Table 21.1.6.

Catechol and  $\text{CO}_2$  are the main decomposition products of quercetin. Other compounds found in the pyrolysate include 2,4-pentanedione and substituted mono-, di-, and trihydroxybenzenes. The source of hydroxybenzenes can be either 3,4-dihydroxyphenyl or chromen moiety.

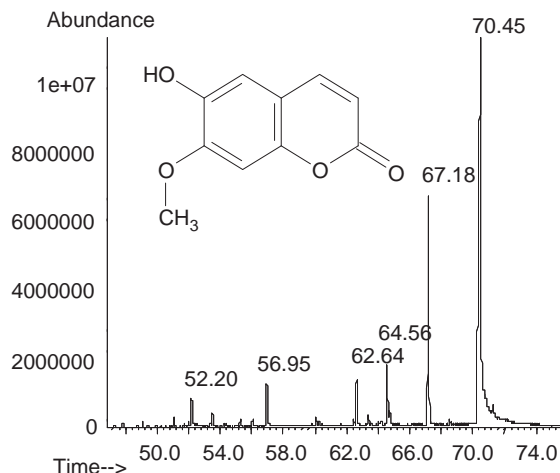


FIGURE 21.1.2. Time window 45–75 min from the pyrogram obtained at  $900^\circ\text{C}$  for scopoletin (MW = 192). Peak assignment in Table 21.1.5.



TABLE 21.1.5. Peak identification as a function of retention time for the pyrogram of scopoletin (whole pyrogram) ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.58	44	124-38-9	<b>15.26</b>
2	Propanone	9.77	58	67-64-1	1.80
3	3',4'-(Methylenedioxy)acetophenone?	51.07	164	3162-29-6	0.64
4	3-Methoxy-1,4-benzenediol	52.20	140	824-46-4	2.82
5	7-Methoxychroman-2-one	53.51	178	N/A	0.59
6	Impurity*	56.95	—	N/A	—
7	7-Methoxychromen-2-one	60.09	176	N/A	0.59
8	7-Methoxy-6-methylchromen-2-one	62.64	190	N/A	2.78
9	2-Allyl-5-ethoxy-4-methoxyphenol	64.56	208	1000122-70-7	2.98
10	3-(4-Hydroxy-3-methoxyphenyl)-2-propenoic acid (ferulic acid)	64.71	194	1135-24-6	0.65
11	6,7-Dimethoxy-2H-1-benzopyran-2-one	67.18	206	120-08-1	<b>15.74</b>
12	7-Hydroxy-6-methoxy-2H-1-benzopyran-2-one (scopoletin)	70.45	192	92-61-5	<b>56.15</b>

Note: Numbers in bold from this and subsequent tables indicate the major pyrolysis constituents.

\*The impurity in the pyrogram at 56.95 min is levoglucosan.

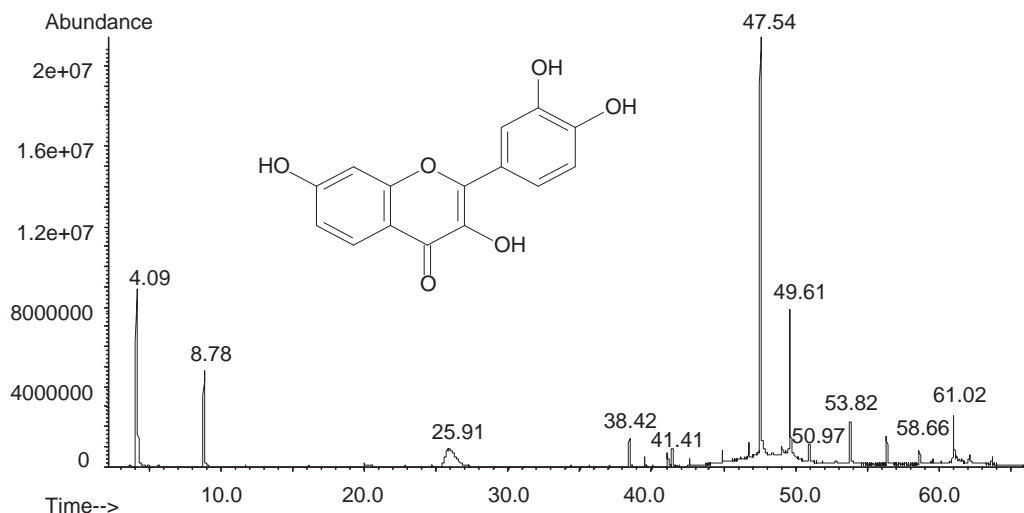


FIGURE 21.1.3. Pyrogram obtain at 900 °C for quercetin. Peak assignment in Table 21.1.6.

The compound with two benzene rings condensed with a  $\gamma$ -pyran is known as xanthene (9-H-xanthene). This compound does not have an aromatic heterocyclic system and was discussed together with chromane in Section 10.5. Among the compounds containing two oxygen atoms in a cycle, there are various derivatives of dioxolane and 1,3- and 1,4-dioxane. These compounds do not have a typical aromatic character and were also discussed in Section 10.5.

For larger molecules containing the  $\alpha$ - or  $\gamma$ -pyrone moiety, various compounds are generated by pyrolysis. As an example, pyrolysis of ellagic acid takes place only at temperatures above 550 °C, leading to the formation of  $CO_2$ , catechol, and a large proportion of char. The formation of catechol in this pyrolysis is not a desirable effect, since ellagic acid is present in many fruits and vegetables and

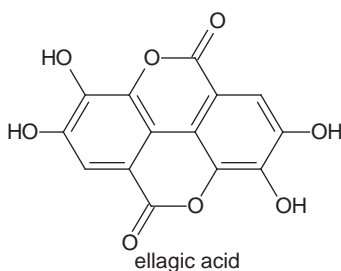
TABLE 21.1.6. Peak identification as a function of retention time for the pyrogram of quercetin ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.09	44	124-38-9	<b>36.83</b>
2	Acetone	8.78	58	67-64-1	<b>8.41</b>
3	Acetic acid	20.03	60	64-19-7	1.79
4	2,4-Pentanedione	25.91	100	123-54-6	<b>10.75</b>
5	Phenol	38.42	94	108-95-2	1.46
6	2-Methoxyphenol	39.47	124	90-05-1	0.43
7	4-Methylphenol	41.07	108	106-44-5	0.49
8	1,3-Benzodioxol-2-one	41.41	136	2171-74-6	0.72
9	2-Methoxy-5-methylphenol	42.59	138	1195-09-1	0.42
10	4,7-Dihydro-1,3-isobenzofurandione	44.92	150	4773-89-1	0.39
11	2-Propoxyphenol	46.73	152	6280-96-2	0.39
12	1-(2-Hydroxy-6-methoxyphenyl)ethanone?	47.20*	166	703-23-1	2.57
13	1,2-Benzenediol (catechol)	47.54	110	120-80-9	<b>20.81</b>
14	6-Hydroxy-4-methoxy-2,3-dimethylbenzaldehyde	48.85*	180	34883-12-0	2.37
15	4-Methyl-1,2-benzenediol	49.61	124	452-86-8	<b>6.70</b>
16	1,3-Benzenediol (resorcinol)	50.97	110	108-46-3	0.89
17	2,4-Dihydroxybenzeneacetic acid?	53.82	168	N/A	1.54
18	Impurity**	56.95	—	N/A	—
19	2,5-Dihydroxybenzeneacetic acid?	58.66	168	451-13-8	0.54
20	2,4,6-Trihydroxybenzoic acid	61.02	170	83-30-7	<b>2.51</b>

\*Peaks at 47.20 and 85.85 min are broad and unresolved.

\*\*The impurity in the pyrogram at 56.95 min is levoglucosan.

catechol is a recognized carcinogen. However, the temperatures necessary for this decomposition are not typically achieved during food processing.



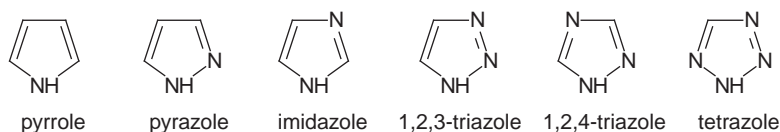
Other reports on pyrolysis products of several compounds with a pyrane ring and various substituents are available in the literature [15–17].

## 21.2. AROMATIC HETEROCYCLES CONTAINING NITROGEN

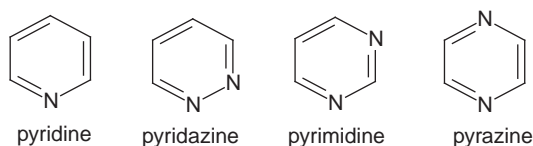
### General aspects

A variety of aromatic heterocyclic rings contain nitrogen as heteroatom. The five-atom rings may contain one nitrogen (pyrrole), two nitrogens (imidazole and pyrazole), three nitrogens (1,2,3-triazole and 1,2,4-triazole), or four nitrogens (tetrazole). The formulas of nitrogenous heterocycles with five-atom rings are

shown below:



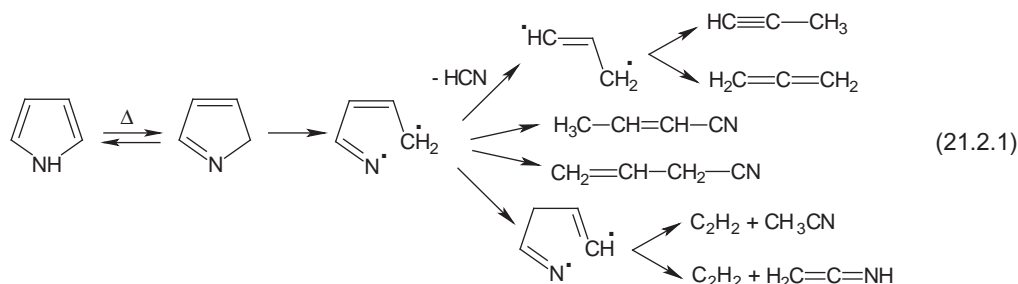
Compounds with six-atom rings can have one nitrogen (pyridine), two nitrogens (pyridazine, pyrimidine, and pyrazine), three, or four nitrogens. The aromatic compounds with one or two nitrogens in a six-atom ring are shown below:



Many natural compounds contain carbon aromatic cycles condensed with those containing nitrogen atoms such as indole (2,3-benzopyrrole), isoindole, carbazole (dibenzopyrrole), benzimidazole, chinoline, acridine, etc. Also, two or more heterocycles can be found in condensed bi- or multicyclic compounds such as purine (imidazole–pyrimidine) pteridine, etc. Only a few of these compounds are discussed in this section as examples.

### Pyrrole

Pyrrole pyrolysis has been evaluated under various conditions. Under continuous flow conditions at 850 °C, there were about 40 decomposition products identified in the pyrolysate [18]. Supportive results were reported regarding the composition of gaseous pyrolysis products of pyrrole [1,19]. Shock wave experiments were conducted in the temperature range 1050–1450 K [20] and 1050–1700 K [21]. In both studies, *cis*-crotonitrile, allylcyanide, hydrogen cyanide, and propyne were found as main products. At higher pyrolysis temperatures, *trans*-crotonitrile was also found. Decomposition products at lower levels included acetylene, ketene imine, acetonitrile, and allene. Fragmentation of pyrrole was found to be initiated by a 1,2-hydrogen shift generating 2H-pyrrole, which undergoes a N–C cleavage to generate a biradical that continues the reaction chain, as shown in the following scheme:



A series of condensation reactions were found to take place during pyrrole pyrolysis in a continuous flow experiment performed at 900 °C [22]. The results regarding percentage compounds in the condensate generated in these conditions are shown in Table 21.2.1.

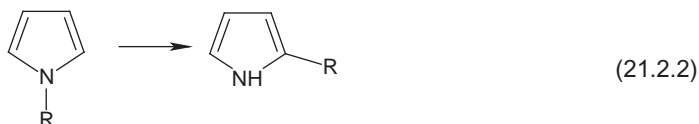
The formation of condensation products can be explained by various interactions of the compounds with high unsaturation among themselves and with the pyrrole present in the pyrolysis products. The

TABLE 21.2.1. Percent of various compounds in the pyrolysis condensate of pyrrole in a continuous flow experiment at 900 °C [22]

No.	Compound	%
1	Benzonitrile	24.1
2	Naphthalene	20.6
3	1-Cyanonaphthalene	15.8
4	Pyrrole	11.6
5	Quinoline	5.9
6	Phenanthrene	5.8
7	Pyrene	5.4
8	Fluoranthene	3.9
9	Acenaphthylene	3.6
10	Indole	3.4
11	9-Cyanoanthracene	< 0.1
12	3-Cyanofluoranthene	< 0.1
13	Acridine	< 0.1
14	Pyridine	< 0.1
15	Carbazole	< 0.1
16	Isoquinoline	< 0.1

mechanism of pyrrole pyrolysis has also been evaluated theoretically with density function theory [23], with results in agreement with the mechanisms indicated by reaction 21.2.1.

N-substituted pyrroles have the tendency to change by pyrolysis into C-substituted compounds (when the substituent is alkyl, aryl, or acyl). The reaction is shown below:



The reaction was reported in the literature for several substituents such as *N*-methyl-, *N*-phenyl-, *N*-benzoyl-, etc. [24]. Some N-substituted compounds lead to the formation of a mixture of  $\alpha$ - and  $\beta$ -substituted isomers with the  $\alpha$  isomer in larger proportion. The change of *N*-methylpyrrole into  $\alpha$ -methylpyrrole is also associated with about 10% change of the compound into pyridine.

### Indole and carbazole

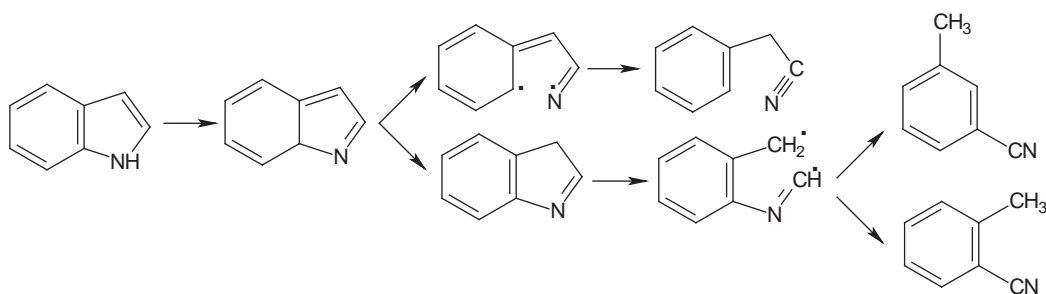
A shock wave experiment on indole (2,3-benzopyrrole) was performed in the temperature range 800–1400 °C [25]. Three main pyrolysis products were found as results of the opening of the pyrrole ring: phenylacetonitrile, and 2- and 3-methylbenzonitrile. Other pyrolysis products, particularly generated at higher temperatures, included C<sub>2</sub>H<sub>2</sub>, HCN, 1,3-butadiene, benzonitrile, acetonitrile, and benzene, as well as low levels of toluene [26,27]. A study performed at 900 °C in a continuous flow pyrolysis experiment evaluated, in addition to the main pyrolysis products generated in a shock wave experiment, a number of condensation compounds, which are listed in Table 21.2.2 [22].

Various condensation reactions are responsible for the formation of larger molecules, which, as seen from Table 21.2.2, include several PAHs such as anthracene, fluorene, fluoranthene, and benzo[*a*]pyrene, and PHAs such as acridine and benzo[*b*]carbazole. The mechanism of indole pyrolysis has been evaluated theoretically, with density function theory, particularly related to the formation of 2-, 3-methylbenzonitrile and phenylacetonitrile [23]. The results showed that the resonance energy in the benzene ring of indole is smaller than the resonance energy in benzene itself, and the

TABLE 21.2.2. Percent of various compounds in the condensate of indole pyrolysate in a continuous flow experiment at 900 °C [22]

No.	Compound	%
1	Indole	41.8
2	Benzonitrile	13.1
3	Phenanthrene	9.7
4	Biphenyl	6.7
5	9-Cyanoanthracene	5.2
6	Quinoline	4.4
7	Anthracene	3.5
8	2-, 3-Methylbenzonitrile and phenylacetonitrile	2.8
9	Carbazole	2.5
10	Naphthalene	2.2
11	Benzo[a]pyrene	1.9
12	Fluoranthene	1.7
13	Fluorine	1.5
14	Isoquinoline	1.0
15	2-Cyanomethylbenzonitrile	0.8
16	Acridine	0.6
17	3-Phenylindole	0.6
18	Benzo[b]carbazole	<0.1

pyrolytic process probably takes place as indicated in the following set of reactions:



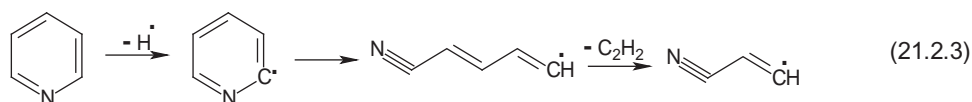
The N-substituted indoles behave similarly to N-substituted pyrroles, and pyrolysis occurs with the transfer of the substituent to a carbon atom. Also, the formation of a six-atom cycle is seen for  $\alpha$ -methylindole, which upon heating around 700 °C generated quinoline. 3-Methylindole (skatole) at elevated temperatures generates a mixture of compounds containing indole.

Pyrolysis of carbazole (dibenzopyrrole, 9-azafluorene) in a similar study as those performed for pyrrole and indole in a continuous flow experiment [22] showed that the compound is very stable to elevated temperatures. Even at 900 °C, only 1.3% naphthalene, HCN, and traces of some condensation products with masses corresponding to a dimer, a trimer, and a tetramer were detected in carbazole pyrolysate. The formation of a six-atom ring is the main reaction during pyrolysis of N-methyl carbazole, which does not have a free position on  $\alpha$ - or  $\beta$  carbons.

### Pyridine

Several studies were performed on pyridine pyrolysis in a continuous flow system [19,22,28]. For the temperature range between 825 °C and 850 °C, the main pyrolysis products were quinoline, benzonitrile,

acetonitrile, acrylonitrile, benzene, and a nonvolatile residue [28]. For a pyrolysis in the range 850–1000 °C, only HCN was an additional pyrolysis product. The largest amount of nitrogen-containing products was found at 985 °C, and most nitrogen-free products were formed above 1000 °C [19]. The formation of HCN is likely not the first step in pyridine pyrolysis, its generation being the result of further cleavage of the initial pyrolysis products [29,30]. Other studies were performed with the attempt to elucidate the mechanism of pyridine pyrolysis [31,32]. One of these studies [31] used, for this purpose, IR laser pyrolysis and showed the formation of smaller molecules such as HCN, C<sub>2</sub>H<sub>2</sub>, cyanoacetylene, acrylonitrile, but-3-ene-1-yne, 1,3-butadiyne, propyne, allene, and ketene imine. Pyridine pyrolysis starts with a C–H cleavage to form pyridyl free radicals with the unpaired electron at the carbons in positions 2, 3, or 4. The formation of free radicals on 4-position of pyridine seems to be the origin of char formation. The scheme of pyridine pyrolysis with the formation of a free radical on 2-position is shown below:



The free radicals formed in reaction 21.2.3 react further leading to a multitude of condensed compounds. The analysis of the condensate from the pyrolysis at 900 °C in a continuous flow system [22] showed the presence of the compounds listed in Table 21.2.3.

TABLE 21.2.3. *Pyrolysis products in the condensate generated at 900 °C from pyridine [22]*

No.	Compound	%
1	Naphthalene	15.0
2	Quinoline	11.8
3	Benzonitrile	8.8
4	1-Cyanonaphthalene	8.1
5	Phenanthridine	6.3
6	9-Cyanoanthracene	6.2
7	Cyanopyridine	5.7
8	Pyridine	5.3
9	Benzo[ <i>h</i> ]quinoline	4.7
10	Phenanthrene	4.4
11	Isoquinoline	3.6
12	$\alpha,\alpha$ -Bipyridine	3.6
13	Cyanoquinoline/isoquinoline	3.4
14	Acenaphthylene	3.0
15	Indole	2.8
16	Fluoranthene	2.7
17	Pyrene	2.1
18	Carbazole	1.5
19	Triphenylene or chrysene	1.4
20	2-Phenylpyridine	1.4
21	Biphenyl	0.8
22	Benzo[ <i>b</i> ]acridine	0.6
23	Fluorine	0.5
24	Phenylquinoline	0.5
25	Phenyl-naphthalene	0.4

As shown in Table 21.2.3, a number of PAHs and condensed other cycle compounds can be found in pyridine pyrolysate. The formation of pyridyl radicals, other free radicals, and acetylene can explain the presence of these compounds.

$\alpha$ -Methylpyridine behaves similarly to pyridine during pyrolysis, and depending on the temperature, the compound with the highest yield is dimethyl- $\alpha,\alpha$ -bipyridine.

### Quinoline and isoquinoline

Both quinoline (1-azanaphthalene) and isoquinoline (benzo[c]pyridine) are compounds very stable to elevated temperatures. The results of quinoline and isoquinoline pyrolysis evaluated in a continuous flow system at 950 °C [33] showed the presence, in the pyrolysate, of benzene, toluene, naphthalene, phenanthrene, and anthracene, as well as the isomer of the other quinoline, indole, and several nitriles including benzonitrile, and several isomers of cyanostyrene, and cyanonaphthalene. The isomerization quinoline/isoquinoline was not confirmed in a different study [19]. A shock wave experiment at temperatures between 1275 K and 1700 K [34] indicated as the main components in the pyrolysate acetylene, benzonitrile, cyanoacetylene, benzene, HCN, phenylacetylene, and 1,3-butadiyne. Also traces of C<sub>6</sub>H<sub>4</sub> (3-hexen-1,5-diyne), pyridine, and ethynylpyridine were found in the pyrolysate. The pyrolysis is likely to occur by C–H cleavages with a higher proportion of formation of free radicals having the unpaired electrons on the carbon atoms ring. These free radicals continue the decomposition reaction by breaking the aromatic rings either with C–C or C–N cleavages. An additional study was performed with continuous flow pyrolysis at 900 and 1100 °C for quinoline and at 900 °C for isoquinoline,

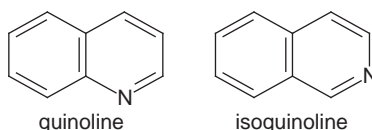
TABLE 21.2.4. *Pyrolysis products in the condensate generated at 900 °C and 1100 °C from quinoline [22]*

No.	Compound	%	
		900 °C	1000 °C
1	Quinoline	35.7	32.3
2	Naphthalene	10.3	13.6
3	Phenanthrene	9.2	
4	Isoquinoline	7.5	
5	Benzonitrile	6.4	14.8
6	9-Cyanoanthracene	4.6	
7	Benzene	4.4	
8	Benzo[b]acridine	3.6	
9	Fluoranthene	3.5	9.6
10	Biphenyl	2.7	3
11	1-Cyanonaphthalene	2.6	3.1
12	Cyanoquinoline/isoquinoline	2.5	
13	Phenylquinoline	1.6	
14	Triphenylene or chrysene	1.5	
15	Pyrene	1.4	10.1
16	Indole	1.3	
17	Acridine	1.2	
18	Anthracene	1.1	5.8
19	Acenaphthylene	0.8	7.6
20	Phenyl naphthalene	0.7	
21	Benzo[c]carbazole	0.6	
22	Fluorine	0.5	
23	Indene	0.3	
24	Benzo[a]pyrene	<0.1	

TABLE 21.2.5. Pyrolysis products in the condensate generated at 900 °C from isoquinoline [22]

No.	Compound	%
1	Naphthalene	15
2	Anthracene	14.4
3	Quinoline	13.2
4	Isoquinoline	11.1
5	Benzonitrile	8.8
6	Fluoranthene	7.6
7	9-Cyanoanthracene	5.4
8	Biphenyl	5
9	1-Cyanonaphthalene	4.3
10	Triphenylene or chrysene	2.6
11	Pyrene	2.1
12	Phenanthridine or acridine	1.9
13	Phenanthrene	1.5
14	Benzo[ <i>b</i> ]acridine	1.5
15	Benzo[ <i>a</i> ]pyrene	1.4
16	Acenaphthylene	1.3
17	Phenyl naphthalene	1.3
18	Fluorine	0.7
19	Indole	0.5
20	Phenylquinoline	0.4

and determined the proportion of various compounds in the pyrolysate. These results are shown in Table 21.2.4 for quinoline and in Table 21.2.5 for isoquinoline [22].



As shown in Tables 21.2.4 and 21.2.5, several PAHs were generated during quinoline and isoquinoline pyrolysis. In addition, a nonvolatile residue was reported in the pyrolysis of both compounds. Some oligomers of the parent compounds were identified in this residue. Pyrolysis of quinoline and isoquinoline, as well as that of pyrrole, indole, carbazole, and pyridine, generated similar molecular fragments indicating similar decomposition paths [22].

Compounds with two aromatic cycles of carbon atoms condensed with a pyridine ring include acridine (10-azaanthracene, 2,3,5,6-dibenzopyridine) and phenanthridine (benzo[*c*]quinoline). Their pyrolysis is expected to be similar to that of quinoline.

### Nicotine

Nicotine (S)-3-(1-methyl-2-pyrrolidinyl)pyridine is an alkaloid found in plants from Solanaceae family, particularly in *Nicotiana tabacum* (tobacco), which can have nicotine in the range 0.6–4% (or even higher). The compound is stable to relatively high temperatures and distills before decomposing. Pyrolysis of this compound was performed on 0.2 mg material in a Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900\text{ °C}$ ,  $\beta = 10\text{ °C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280\text{ °C}$ . The analysis of pyrolysate was done exclusively by GC/MS under conditions given in Table 4.6.1. The time window between 35 min and 65 min from the pyrogram is shown in Figure 21.2.1, and the peak identification is given in Table 21.2.6.



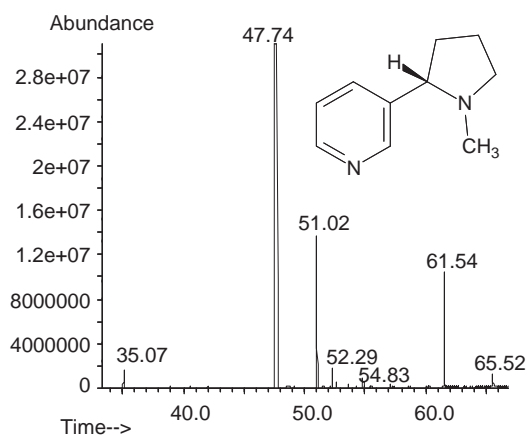


FIGURE 21.2.1. Time window 35–65 min from the pyrogram obtained at 900 °C for nicotine (MW = 162).

TABLE 21.2.6. Peak identification as a function of retention time for the pyrogram of nicotine in Figure 21.2.1 ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	3-Vinylpyridine	35.07	105	1121-55-7	0.49
2	3-Pyridinecarboxaldehyde	38.11	107	500-22-1	0.01
3	3-Pyridinecarbonitrile	38.85	104	100-54-9	0.05
4	2-Isocyanatopyridine	40.55	120	4737-19-3	0.03
5	1-(3-Pyridinyl)ethanone	41.97	121	350-03-8	0.02
6	(S)-3-(1-Methyl-2-pyrrolidinyl)pyridine (nicotine)	47.74	162	54-11-5	<b>92.41</b>
7	1-(4-Pyridinyl)ethanone	48.67	121	1122-54-9	0.01
8	3-(3,4-Dihydro-2H-pyrrol-5-yl)pyridine (myosmine)	51.02	146	532-12-7	<b>3.06</b>
9	3-(1-Methyl-1H-pyrrol-1H-2-yl)pyridine ( $\beta$ -nicotyrine)	52.29	158	487-19-4	0.38
10	3-(1,4-Dimethylpyrrol-2-yl)pyridine	52.65	172	N/A	0.08
11	N-Methyl-3-pyridinecarboxamide	54.83	136	114-33-0	0.21
12	1-Acetyl-2-(3-pyridyl)pyrrolidine	57.07	190	N/A	0.01
13	(S)-1-Methyl-5-(3-pyridinyl)-2-pyrrolidinone (cotinine)	61.54	176	486-56-6	<b>2.80</b>
14	N-Formylornicotine	65.52	176	3000-81-5	0.44

As shown in Table 21.2.6, nicotine represents more than 92% of the pyrolysate in the conditions of flash pyrolysis at 900 °C. A few oxygenated compounds (including cotinine) were generated in the pyrolysate due to the presence of traces of oxygen in the pyrolysis atmosphere. Traces of cotinine and myosmine were present in the initial nicotine sample, but at lower levels compared to those in the pyrolysate. It is likely that several reactions take place during pyrolysis of nicotine, one of them being elimination of  $CH_4$  as shown below:

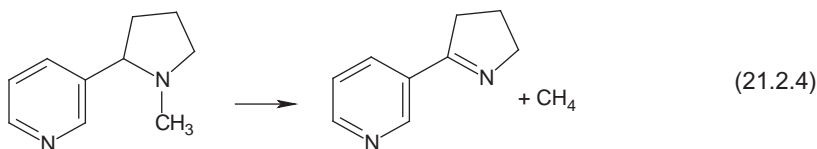


TABLE 21.2.7. Nicotine pyrolysis products at 860 °C in N<sub>2</sub> and extended heating time [40]

No.	Compound	Percentage in pyrolysate
1	Pyridine	5.3
2	2-Methylpyridine	0.51
3	3-Methylpyridine	8.1
4	3-Vinylpyridine	1.0
5	2-Cianopyridine	25.3
6	2- and/or 4-cyanopyridine	7.19
7	Quinoline	7.2
8	Isoquinoline	1.3
9	Nicotine	16.4
10	Benzene	0.40
11	Pyrrole	1.2
12	Toluene	0.3
13	Benzonitrile	0.69
14	Indole	1.2
15	Skatole	0.25

Besides the formation of different nicotine pyrolysis products, racemization in the range 2.6–3.6% of the stereoisomer *S*-nicotine into the *R*-form was reported [35]. Various other studies were performed on nicotine pyrolysis [36–39]. When the sample is not allowed to volatilize and is pyrolyzed at 860 °C for an extended period of time in N<sub>2</sub>, the reported pyrolysis products are as shown in Table 21.2.7 [40].

Some results regarding pyrolysis of nicotine on different supports such as SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> were discussed in Section 2.6.

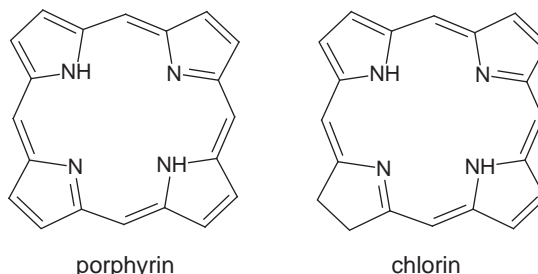
### Simple heterocycles with more nitrogen atoms

The aromatic heterocycles with five or six atoms including two nitrogens are very stable compounds to elevated temperatures. Subject to flash pyrolysis in conditions similar to Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900$  °C, imidazole, pyrazole, and pyrazine, for example, did not show any detectable decomposition. However, pyrolysis of such compounds at higher temperatures is reported in the literature (see, e.g., [41]). Pyrazine and pyrimidine pyrolysis in a shock wave experiment was performed in the temperature range 1680–2300 K with 2% and 4% pyrazine in Kr, and in the temperature range 1460–2667 K with 2% pyrazine in Ar/Ne inert atmosphere [41]. The pyrolysis reaction starts with a C–H bond cleavage. The study estimated a bond dissociation energy of 105 kcal/mol for pyrazine and 99 kcal/mol for the C–H dissociation in pyrimidine. Pyrazinyl free radicals continue the dissociation with the opening of the aromatic ring and formation of fragment molecules such as CH≡C–C≡N. Specific kinetic parameters are reported for individual reactions in pyrazine pyrolysis process. A set of 35 chemical reactions were used to model pyrazine pyrolysis [41]. Substituted compounds of imidazole, pyrazole, and pyrazine with alkyl or aryl groups are less stable. Both pyrazole and imidazole can form quaternary salts (e.g., imidazolium halides). Pyrolysis of imidazolium halides typically leads to 1-substituted imidazoles [42,43].

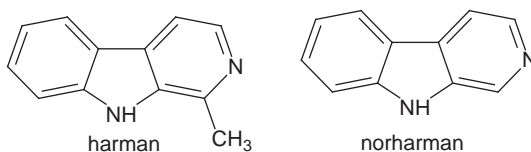
### Other heterocycles containing nitrogen

Other heterocycles containing nitrogen are known and some are common in nature. One example is the group of compounds related to porphyrin. This group has an aromatic character containing  $4n+2 = 22$  ( $n = 5$ )  $\pi$  electrons and has a strong delocalization of the double bonds that are usually pictured in porphyrin formula. Porphyrin has the capability to form stable complexes with metal ions such as Mg<sup>2+</sup>,

$\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ , and  $\text{V}^{3+}$ , the metal replacing the two hydrogens from two porphyrin nitrogens and forming coordinate bonds with the other two nitrogens (in case of  $\text{Fe}^{3+}$  in hemine, the complex has a positive charge and a counterion such as  $\text{Cl}^-$ ). The porphyrin nucleus is present in hemoglobin. Chlorophyll, the green pigment in most plants, contains a slightly different moiety than porphyrin. This moiety is chlorin, which has three indole units and one pyrrole unit (one double bond in a pyrrole is replaced by a single bond).

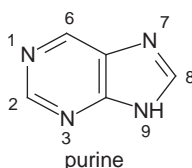


Heterocyclic rings can be present in condensed polycyclic compounds with more than one heterocycle and possibly with carbon aromatic rings. For example, a pyrazine ring condensed with a benzene ring leads to quinoxaline, and condensed with two benzene rings generates phenazine. Heterocyclic systems with one benzene ring and two pyridine rings lead to *o*-, *m*-, or *p*-phenanthroline. Other compounds have two condensed heterocyclic rings such as harman and norharman. These compounds are stable to heating. Subjected to flash pyrolysis in conditions similar to Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ , harman and norharman did not show any detectable decomposition.



The compounds with more nitrogen atoms tend to generate, by pyrolysis at higher temperatures, simpler heterocycles. For example, flash vacuum pyrolysis of 1-vinylbenzotriazole generates indoles and also benzonitrile and *N*-phenylketenamine [44].

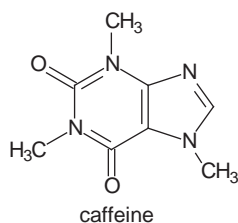
One group of compounds of considerable importance, because of their presence in nature, is made by the derivatives of purine (imidazo-pyrimidine). Purine itself has a pronounced aromatic character and is stable to pyrolysis. Related to purine are several important natural compounds such as adenine and guanine, which are bases in nucleic acids; important biomolecules such as adenosine, adenosine triphosphate (ATP), adenosine diphosphate (ADP), cyclic adenosine monophosphate (cycAMP), coenzyme A; and natural compounds such as caffeine, theobromine, and uric acid.



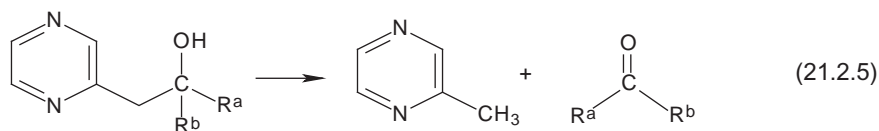
Besides the few examples previously indicated, nitrogen-containing heterocyclic compounds with condensed rings are common in many natural and synthetic compounds, including vitamins (e.g., riboflavin), alkaloids (papaverine, lysergic acid, yohimbine, reserpine, etc.), and pharmaceutical drugs.

**Nitrogen-containing heterocycles with additional functionalities**

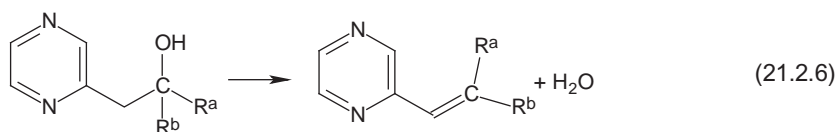
Numerous compounds with nitrogen-containing aromatic rings have additional functionalities in the molecule. Some of these heterocyclic compounds are very resistant to heating. As an example, caffeine does not show any noticeable decomposition when subjected to flash pyrolysis in conditions similar to Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900^\circ\text{C}$ .



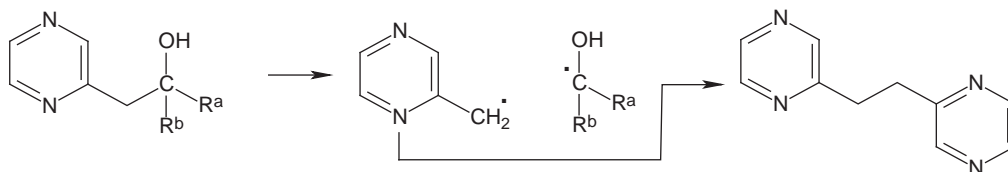
Pyrolysis of other heterocyclic compounds containing one specific type of substituent (such as  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{NH}_2$ , etc) was previously discussed in this book. Many pyrolysis reactions for these compounds take place following reaction paths which do not affect the aromatic heterocycle and with the decompositions involving the functional group in a similar way as in the case of compounds having those specific functionalities on a carbon aromatic ring. One example is offered by the pyrolysis of several pyridylethanols and pyrazylethanols. The work was performed in relation to the transformation of pyridines and pyrazines during cooking or roasting [45]. One typical reaction for 1-pyrazyn-2-ylalkan-2-ols takes place as shown below:



Reaction 21.2.5 is similar to reaction 9.1.10 of secondary alcohols. The reaction with water elimination typical for some alcohols also takes place and generates alkenes, as shown in the following reaction:



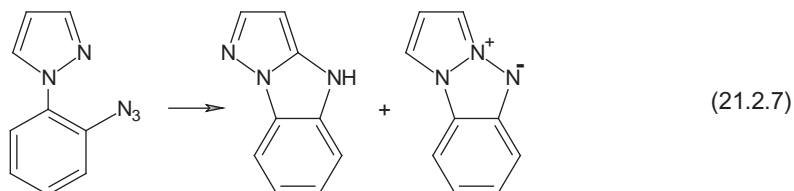
In addition to these two main pyrolysis reactions, the formation of 1,2-dipyrazylethanes was detected for some pyrazylethanols. The formation of these compounds probably takes place by a radicalic mechanism as shown below:



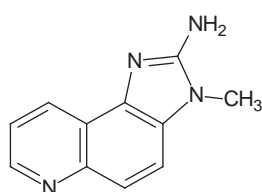
Similar reactions to 21.2.5 and 21.2.6 were proven for pyrazylethanols with different substituents and for 1-(2-pyridyl)alkane-2-ols [45].

Specific reactions were used for the synthesis of certain nitrogenous heterocycles. One such example is shown in the following reaction that takes place in flash vacuum pyrolysis of

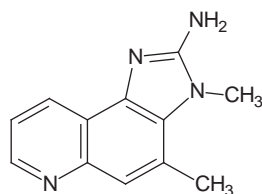
(2-azidophenyl)pyrazole [46]:



A number of heterocyclic compounds containing amino groups and possibly other functionalities such as  $\text{-OH}$  are of particular interest for their biological activity (particularly as carcinogens). Some of these compounds were identified in food as a result of elevated temperatures generated in particular during broiling and frying [47–50]. These compounds contain different heterocyclic structures and can be classified as amine derivatives of these heterocycles. Two quinoline derivatives are shown below:

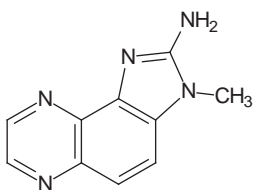


2-amino-3-methylimidazo[4,5-f]-quinoline, (IQ) from broiled sardines

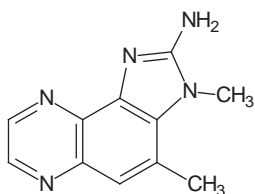


2-amino-3,4-dimethylimidazo[4,5-f]-quinoline (MeIQ) from broiled sardines

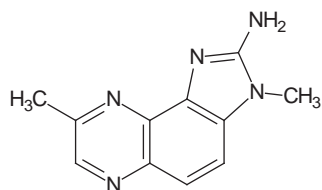
Several heterocyclic amines are derivatives of quinoxaline:



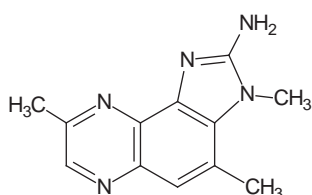
2-amino-3-methylimidazo[4,5-f]quinoxaline (IQx)



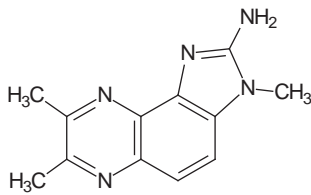
2-amino-3,4-dimethylimidazo[4,5-f]-quinoxaline (4-MeIQx) from fried beef



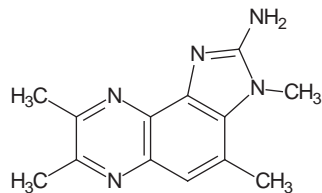
2-amino-3,8-dimethylimidazo[4,5-f]-quinoxaline (8-MeIQx) from fried beef



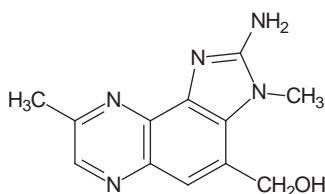
2-amino-3,4,8-trimethylimidazo[4,5-f]-quinoxaline (4,8-diMeIQx) from fried beef



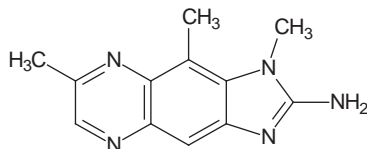
2-amino-7,8-trimethylimidazo[4,5-f]-quinoxaline (7,8-diMeIQx) from fried beef



2-amino-3,4,7,8-tetramethylimidazo[4,5-f]-quinoxaline (triMeIQx)

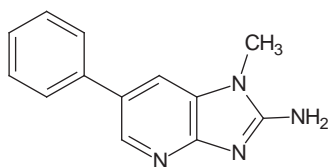


2-amino-4-hydroxymethyl-3,8-dimethylimidazo[4,5-f]quinoxaline, (4-CH<sub>2</sub>OH-8-MelQx)

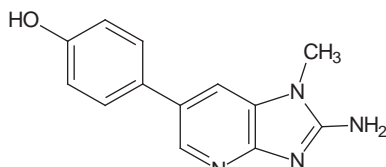


2-amino-1,7,9-trimethylimidazo[4,5-f]quinoxaline 7,9-DiMelgQx

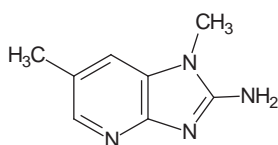
Other heterocyclic amines are derivatives of pyridine:



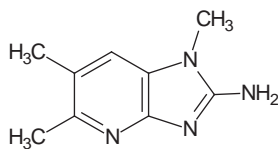
2-amino-1-methyl-6-phenylimidazo[4,5-b]pyridine (PhIP)



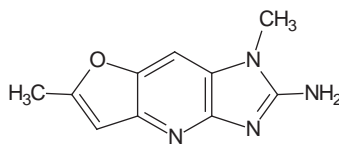
2-amino-1-methyl-6-(4-hydroxyphenyl)imidazo[4,5-b]pyridine (4-OH-PhIP)



2-amino-1,6-dimethylimidazo[4,5-b]pyridine (1,6-DMIP)

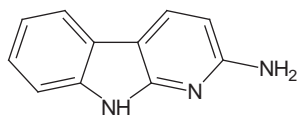


2-amino-1,5,6-dimethylimidazo[4,5-b]pyridine (1,5,6-TMIP)

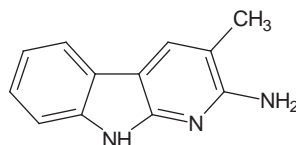


2-amino-1,6-dimethylfuro[3,2-e]imidazo[4,5-b]pyridine (IFP)

Two common heterocyclic amines in food are derivatives of pyridoindole:



2-amino-9H-pyrido[2,3-b]indole (AαC), from soybean globulin pyrolysate



2-amino-3-methyl-9H-pyrido[2,3-b]indole, (MeA αC) from soybean globulin pyrolysate

These compounds are in general resistant to pyrolysis and are formed as a result of complex interactions at elevated temperatures between sugars, amino acids, or proteins, and other food components. Some heterocyclic amines were identified in the pyrolysates of simple amino acids (see Section 18.1). A discussion of toxicological aspects of some heterocyclic amines is given in Section 25.1.

A few examples of pyrolysis results on natural compounds containing nitrogenous heterocycles are given below. The results were obtained in a Type 1 Experiment as described in Section 4.6, at  $T_{eq} = 900^\circ\text{C}$ ,  $\beta = 10^\circ\text{C/ms}$ , THT = 10 s, and housing temperature  $T_{hou} = 280^\circ\text{C}$  with the analysis of pyrolysate done exclusively by GC/MS under conditions given in Table 4.6.1. The first example is that of 2,6-deoxyfructosazine or 2-(D-arabinotetrahydroxybutyl)-6-(D-erithro-2',3',4'-trihydroxybutyl)pyrazine. This compound is common in roasted foods and tobacco, and is formed from the interaction of glucose and ammonia. The pyrogram for this compound is given in Figure 21.2.2, and the peaks identification according to their retention times in Table 21.2.8.

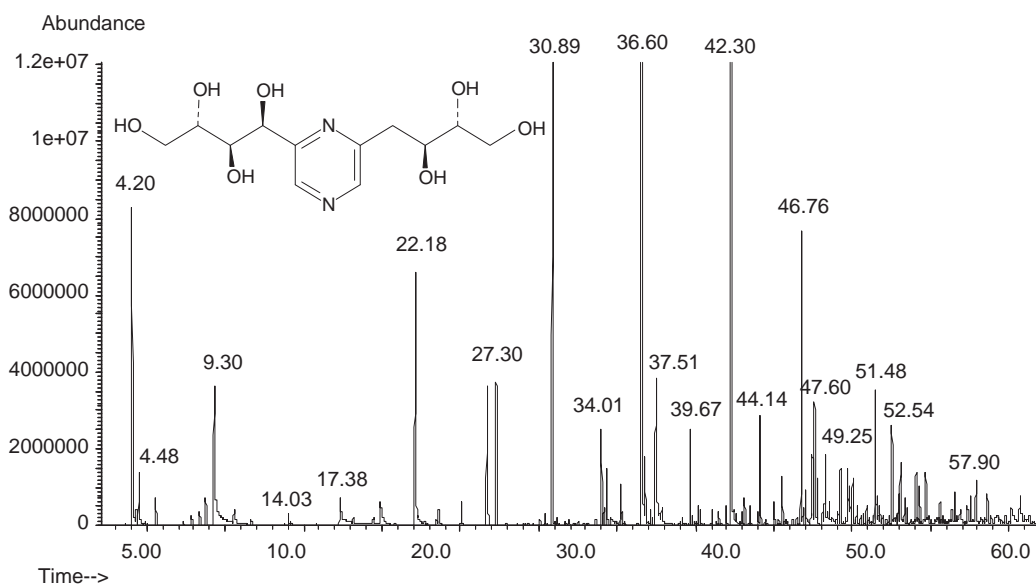
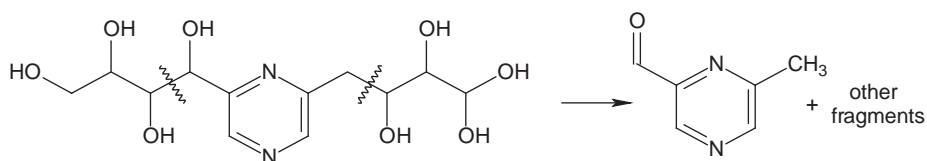


FIGURE 21.2.2. Pyrogram obtained at 900 °C for 2,6-deoxyfructosazine (MW = 304). Peak identification in Table 21.2.8 at page 664.

The formation of 2-butanone is explained by reaction of the form 21.2.5. The formation of 6-methylpyrazyn-2-aldehyde is explained by a reaction as shown below:



In a similar fragmentation, 6-methyl-2-pyrazinylmethanol is generated. The formation of dipyrazylethane was not noticed in 2,6-deoxyfructosazine pyrolysis, and the detection of 2-(2-pyrazyn-2-ylvinyl)pyrazine was only tentative.

Some heterocyclic compounds are part of complex molecules. Porphyrin nucleus, for example, is present in hemoglobin in an assembly of four globular protein subunits. In each subunit, a substituted porphyrin ring known as heme is bound to the protein by a coordinate bond between the  $\text{Fe}^{2+}$  and the nitrogen of a histidine residue (and the sixth coordination site of  $\text{Fe}^{2+}$  is occupied by the oxygen when the hemoglobin is oxygenated). Heme is a very unstable molecule.

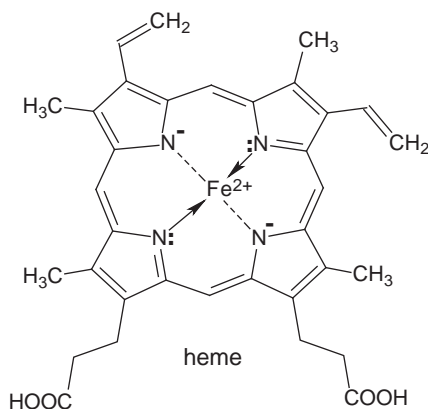


TABLE 21.2.8. Identification of the main peaks in the chromatogram shown in Figure 21.2.2 for the pyrolysis of 2,6-deoxyfructosazine at 900 °C (hydrogen, CO, methane, ethane, water not included)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.20	44	124-38-9	<b>11.32</b>
2	Formaldehyde	4.48	30	50-0-0	2.44
3	Acetone	8.77	58	67-64-1	0.54
4	2-Butanone	9.30	72	78-93-3	<b>4.86</b>
5	Acetic acid vinyl ester	14.04	86	108-05-4	0.37
6	Hydroxyacetaldehyde	17.35	60	141-46-8	0.53
7	Acetic acid vinyl ester	19.89	60	64-19-7	0.53
8	1-Hydroxypropanone	22.18	74	116-09-6	<b>10.19</b>
9	Propanoic acid	25.06	74	79-09-4	0.43
10	2-Methylpyridine	26.70	93	109-06-9	2.27
11	Methylpyrazine	27.30	94	109-08-0	2.76
12	2,6-Dimethylpyrazine	30.89	108	108-50-9	<b>9.64</b>
13	2-Ethyl-6-methylpyrazine	34.01	122	13925-03-6	1.16
14	Trimethylpyrazine	34.17	122	14667-55-1	0.26
15	2-Pyridinecarboxaldehyde	34.35	107	1121-60-4	0.96
16	2-Vinyl-6-methylpyrazine	35.23	120	13925-09-2	0.42
17	5-Methylcarboxaldehyde	35.11	110	620-02-0	0.29
18	6-Methylpyrazine-2-aldehyde	36.60	122	N/A	<b>13.72</b>
19	5-Methylpyrazine-2-aldehyde	36.80	122	N/A	0.84
20	1,3-Dihydroxypropanone	37.51	90	96-26-4	<b>4.85</b>
21	1-(6-Methyl-2-pyrazinyl)-1-ethanone	39.68	136	22047-26-3	1.05
22	2-Methyl-6-(1-propenyl)pyrazine	40.19	134	18217-81-7	0.24
23	2-Methyl-6-butylpyrazine	40.34	150	N/A	0.21
24	2-Ethyl-6-propenylpyrazine	41.06	148	N/A	0.21
25	6-Methyl-2-pyrazinylmethanol	42.30	124	77164-93-3	<b>14.15</b>
26	6-Butadienyl-2-methylpyrazine	44.14	148	N/A	1.05
27	2-Methylquinoxaline	45.54	144	7251-61-8	0.51
28	2-(2'-Furyl)-6-methylpyrazine	46.76	160	N/A	<b>2.79</b>
29	1-(6-Methylpyrazin-2-yl)propan-2-ol	47.05	152	N/A	0.38
30	7,8-Dihydroquinoxaline?	47.46	132	N/A	1.42
31	4-Methylpyrrolo[1.2-a]pyrazine	47.60	132	64608-60-2	1.94
32	6-(But-2-enyl)-2-ethylpyrazine?	47.80	162	N/A	0.48
33	4-(6-Methylpyrazin-2-yl)but-?-en-?-ol	48.28	164	N/A	0.80
34	Unknown	49.25	174	N/A	0.56
35	Unknown	49.72	174	N/A	0.75
36	Quinoxalin-?-ol	50.03	146	N/A	0.58
37	5-(6-Ethylpyrazin-2-yl)-4,5-dihydrofuran?	51.48	176	N/A	<b>1.17</b>
38	Quinoxalin-?-ol	52.54	146	N/A	<b>1.17</b>
39	Unknown	53.07	162	N/A	0.63
40	Unknown	54.08	160	N/A	0.60
41	Unknown	54.29	184	N/A	0.41
42	2-(2-Pyrazyn-2-ylvinyl)pyrazine?	57.90	184	N/A	0.53



Five main types of chlorophylls are found in plants. These include chlorophyll-*a* (the most common), *b*, *c1*, *c2*, and *d*. All chlorophylls contain a  $\text{Mg}^{2+}$  ion bound to the four nitrogens of chlorin and several side chains. Phytol is connected to the chlorin unit in chlorophyll-*a*, *b*, and *d*. A second example for pyrolysis results on natural compounds containing nitrogenous heterocycles is for chlorophyll-*a*. The resulting pyrogram for 0.2 mg chlorophyll-*a* is shown in Figure 21.2.3, and the peak identification is given in Table 21.2.9.

As shown in Table 21.2.9, fragment molecules are generated from both the chlorin ring and phytol side chain. Neophitadiene (the alkene generated from phytol dehydration) is one important component of the pyrolysate. Several substituted pyrroles are also present in the pyrolysate. Due to the high molecular weight and lack of volatility, chlorophyll pyrolysis at 900 °C generated a relatively large proportion of small molecules such as  $\text{CO}_2$ , propene, and 2-methylpropene.

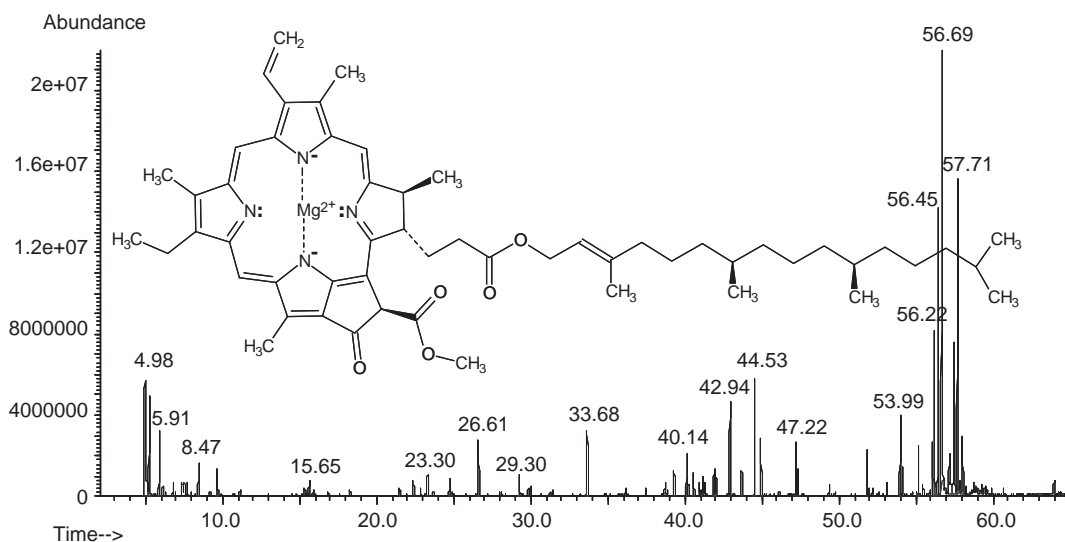


FIGURE 21.2.3. Pyrogram obtained at 900 °C for chlorophyll-*a* (MW = 823).

TABLE 21.2.9. Peak identification as a function of retention time for the pyrogram of chlorophyll-*a* shown in Figure 21.2.3 ( $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{N}_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.98	44	124-38-9	<b>17.53</b>
2	Propene	5.26	42	115-07-1	<b>11.31</b>
3	2-Methylpropene	5.91	56	115-11-7	<b>5.36</b>
4	1,3-Butadiene	6.15	54	106-99-0	1.18
5	3-Methyl-1-butene	6.81	70	563-45-1	0.87
6	1-Pentene	7.54	70	109-67-1	1.15
7	2-Methyl-1-butene	7.73	70	563-46-2	1.10
8	2-Methyl-1,3-butadiene (isoprene)	8.47	68	78-79-5	<b>3.04</b>
9	4-Methyl-1-pentene	9.66	84	691-37-2	1.93
10	1-Methylcyclopentadiene	15.35	80	96-39-9	0.76
11	4-Methyl-1-hexene	15.65	98	3769-23-1	1.06

(Continued)

TABLE 21.2.9. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
12	Benzene	18.27	78	71-43-2	0.78
13	2-Methylheptane	21.43	114	592-27-8	0.30
14	6-Methyl-2-heptene	22.38	112	73548-72-8	0.70
15	5-Methyl-2-heptene	22.87	112	22487-87-2	0.36
16	2-Methyl-1-heptene	23.30	112	15870-10-7	0.93
17	Toluene	24.75	92	108-88-3	1.08
18	2,6-Dimethyl-1-heptene	26.61	126	3074-78-0	<b>2.01</b>
19	3,7-Dimethyl-1-octene	29.30	140	4984-01-4	0.64
20	1,3-Dimethylbenzene	29.87	106	108-38-3	0.47
21	3,6-Dimethyloctane	30.06	142	15869-94-0	0.28
22	2,6-Dimethyl-1-octene	31.42	140	6874-29-9	0.21
23	2,6-Dimethylnonane	33.60	156	17302-28-2	0.20
24	4-Methyldecene	33.68	154	13151-29-6	1.77
25	2,3-Dimethyl-1H-pyrrole	36.14	95	600-28-2	<b>0.36</b>
26	2,3,7-Trimethyldecane	37.47	184	62238-13-5	0.18
27	2,3,4-Trimethyl-1H-pyrrole	38.72	109	3855-78-5	<b>0.54</b>
28	4-Ethyl-2-methyl-1H-pyrrole	39.32	109	5690-96-0	<b>1.11</b>
29	2,6-Dimethylundecane	40.14	184	17301-23-4	0.89
30	1-Cyclopropyloctane?	40.25	154	1472-09-9	0.31
31	3,7-Dimethyl-1-undecene	40.59	182	N/A	0.69
32	2-Butyl-1,1,3-trimethylcyclohexane	40.97	182	54676-39-0	0.27
33	3-Ethyl-2,4-dimethyl-1H-pyrrole	41.06	123	517-22-6	<b>0.24</b>
34	4-Ethyl-2,3-dimethyl-1H-pyrrole	41.22	123	491-18-9	<b>0.73</b>
35	3-Ethyl-2,5-dimethyl-1H-pyrrole	41.33	123	69687-78-1	<b>0.61</b>
36	7-Methyltridecane	41.92	198	26730-14-3	0.50
37	4-Ethyl-2,5-dimethyl-1H-pyrrole	42.02	123	N/A	<b>0.90</b>
38	7-Methyl-6-tridecene	42.94	196	24949-42-6	1.88
39	3-Ethyl-2,4,5-trimethyl-1H-pyrrole	43.70	137	520-69-4	<b>0.88</b>
40	3,7,11-Trimethyl-1dodecene	44.53	210	1189-38-2	2.17
41	2,6,10-Trimethyldodecane	44.96	212	3891-98-3	1.03
42	2,6,10-Trimethyltridecane	47.22	226	3891-99-4	0.89
43	4,8,12-Trimethyl-1-tridecene	47.36	224	N/A	0.47
44	2,3,5-Trimethyl-4-prop-2-enyl-1H-pyrrole	49.38	149	N/A	<b>0.45</b>
45	2,6,10-Trimethylpentadecane	51.84	254	3892-00-0	0.69
46	2,6,10,14-Tetramethylpentadecane	53.13	268	1921-70-6	0.17
47	2,6,10,14-Tetramethylpentadec-1-ene	53.99	266	N/A	1.14
48	2,6,10,14-Tetramethylpentadec-1-ene (stereoisomer)	54.13	266	N/A	0.40

(Continued)

TABLE 21.2.9. *cont'd*

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
49	2,6,10,14-Tetramethylhexadec-2-ene	55.18	280	56554-34-8	0.68
50	2,6,10,14-Tetramethylpentadec-1-ene (stereoisomer)	55.48	266	N/A	0.16
51	7,11-15-Trimethyl-heptadecadiene	56.09	278	N/A	0.92
52	[?-[?-(?)]-3,7,11,15-Tetramethyl-2-hexadecene	56.22	280	N/A	2.29
53	[R-[R,R-(E)]-3,7,11,15-Tetramethyl-2-hexadecene	56.45	280	14237-73-1	4.02
54	Neophytadiene	56.70	278	504-96-1	<b>10.02</b>
55	An eicosadiene	57.18	278	N/A	0.87
56	(E)-2,4-Phytadiene	57.49	278	N/A	<b>2.42</b>
57	Phytol	57.71	296	150-86-7	<b>4.20</b>
58	Heneicosene	57.85	294	N/A	0.29
59	An eicosadiene	58.04	278	N/A	0.87
60	A Heneicosadiene	58.26	292	N/A	0.17
61	A Heneicosadiene	58.76	292	N/A	0.15
62	A Heneicosadiene	59.30	292	N/A	0.16
63	Trimethyltridecylbenzene	63.98	302	N/A	0.26

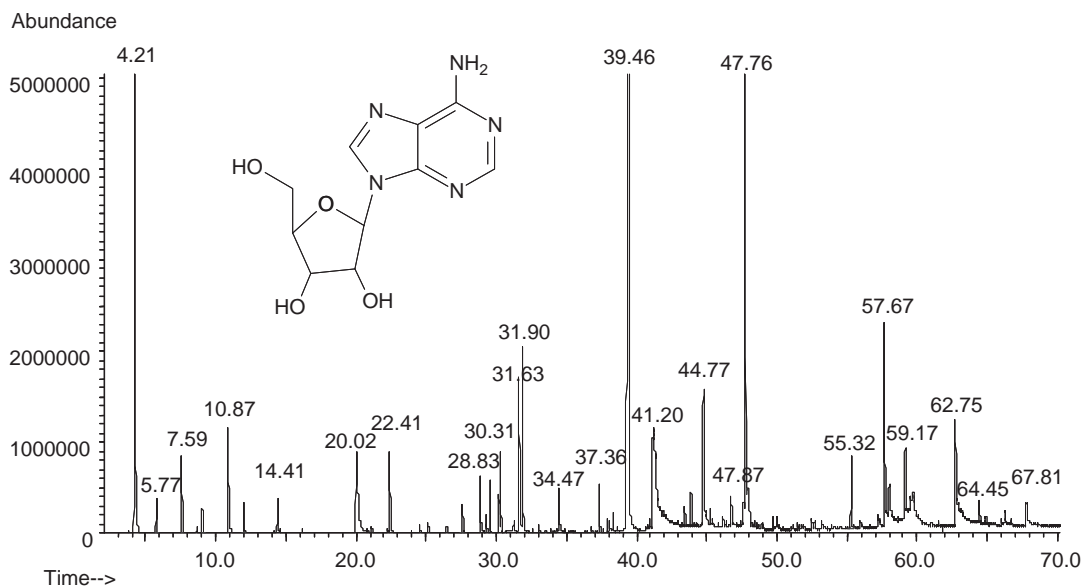


FIGURE 21.2.4. Pyrogram obtained at 900°C for adenosine (MW = 267). Peak assignment in Table 21.2.10.

Another example regarding the pyrolysis of a heterocyclic compound common in nature is that for adenosine or (2R,3R,4R,5R)-2-(6-aminopurin-9-yl)-5-(hydroxymethyl)oxolane-3,4-diol. The molecule of this compound consists of an adenine group attached to a ribofuranose via a  $\beta$ -N9-glycosidic bond. Adenosine plays an important role in biochemical processes, such as energy transfer when the compound is present as ATP or ADP, as well as in signal transduction as cycAMP. The pyrogram obtained from 1.0 mg of adenosine at  $T_{eq} = 900^\circ\text{C}$  and conditions as previously described is given in Figure 21.2.4. The peak assignment following their retention time is given in Table 21.2.10.

Pyrolysis of adenosine shows fragments from both the purine and ribofuranose moieties. Some compounds in the pyrolysate were only tentatively identified, not being present in common mass spectral libraries. One such example is the spectrum of the peak eluting at 39.46 min in adenosine pyrolysate. The compound was tentatively identified as 4,5-dimethyl-imidazolidin-2-one, and the spectrum is shown in Figure 21.2.5.

TABLE 21.2.10. Peak identification as a function of retention time for the pyrogram of adenosine shown in Figure 21.2.4 ( $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{N}_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Carbon dioxide	4.21	44	124-38-9	<b>28.83</b>
2	Acetaldehyde	5.77	44	75-07-0	1.04
3	Furan	7.59	68	110-00-9	1.57
4	Propanal	8.68	58	123-38-6	0.30
5	Acetone	9.05	58	67-64-1	0.71
6	Acetonitrile	10.87	41	75-05-8	<b>6.42</b>
7	2-Methylfuran	12.01	82	534-22-5	0.63
8	2,3-Butandione (diacetyl)	14.41	86	431-03-8	0.66
9	Acetic acid	20.02	60	64-19-7	<b>5.42</b>
10	1-Hydroxy-2-propanone	22.41	74	116-09-6	1.84
11	Propionic acid	25.15	74	79-09-4	0.24
12	2-Pyridinamine	27.60	94	504-29-0	0.56
13	1,4-Dioxadiene	28.83	84	N/A	1.28
14	Methyl-1,4-dioxadiene?	29.57	98	N/A	0.71
15	2-Cyclopentene-1,4-dione	30.20	96	930-60-9	0.51
16	3-Furaldehyde	30.31	96	498-60-2	1.39
17	2-Furanmethanol	31.63	98	98-00-0	2.99
18	1-(Acetoxy)-2-propanone	31.90	116	592-20-1	2.10
19	2-Hydroxy-2-cyclopenten-1-one	34.47	98	547-65-9	0.78
20	6,8-Dioxabicyclo[3.2.1]octane	37.36	114	280-16-0	0.65
21	4,5-Dimethylimidazolidin-2-one?	39.46	114	N/A	<b>19.48</b>
22	Unknown	41.16	142	N/A	4.39
23	2-Methylfuro[2,3-c]pyridine	43.44	133	69022-76-0	0.26
24	Unknown	43.89	142	N/A	0.28
25	4-Pyridinol	44.77	95	1000132-29-2	3.60
26	Unknown	47.76	142	N/A	<b>5.84</b>
27	C5-Anhydrosugar	55.32	142	N/A	0.75
28	6-Methyl-1H-purine	57.67	134	2004-03-7	<b>3.35</b>
29	1H-Purine	58.04	120	120-73-0	0.72
30	6-Ethylpurine?	59.17	148	N/A	0.88
31	Unknown	59.75	195	N/A	0.03
32	9-Allyl-9H-purine-6-carbonitrile	62.75	185	N/A	1.24
33	Adenine	63.12	135	73-24-5	0.04
34	Unknown	64.45	199	N/A	0.22
35	2-Furyl-purin-6-ylamine	67.81	215	525-79-1	0.28

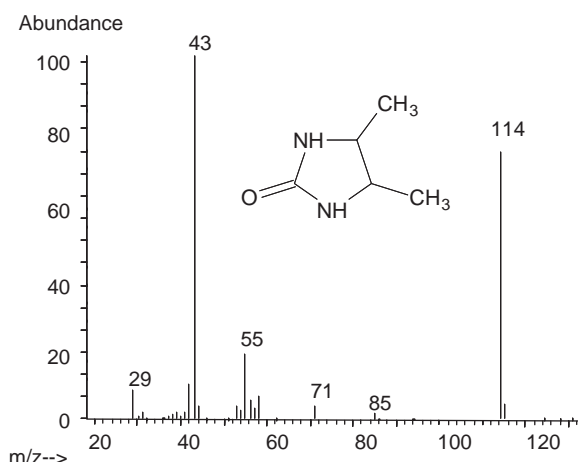


FIGURE 21.2.5. Tentative mass spectrum of 4,5-dimethylimidazolidin-2-one.

Compounds such as acetaldehyde, furan, propanal, acetone, 2-methylfuran, 2,3-butanedione (diacetyl), acetic acid, 1-hydroxy-2-propanone, propionic acid, etc. are results from the sugar moiety of adenosine.

Many other pyrolysis and/or thermal decomposition reactions of compounds with nitrogen-containing heterocycles are reported in the literature (see, e.g., [47–58]).

### 21.3. AROMATIC HETEROCYCLES CONTAINING SULFUR

#### General aspects

The main sulfur-containing heterocyclic compound is thiophene. Its properties are very similar to those of benzene. Benzothiophene has properties similar to naphthalene. Thiophene is used as the starting material for the synthesis of a number of agrochemicals and pharmaceuticals. Thiophene, benzothiophene, and dibenzothiophene are present in crude oil at levels up to 3%, and their elimination is an important step in petroleum processing.

#### Thiophene

Thiophene has a molecule stable to elevated temperatures [59–61], and in conditions of flash vacuum pyrolysis even at 1100 °C, intact thiophene is present. At longer heating time at elevated temperatures, thiophene generates benzene, hydrogen, methane, and hydrogen sulfide as the main pyrolysis products and lower levels of dithiophenes. In an additional study [1], ethylene and acetylene were also reported as pyrolysis products. In other studies [62,6] performed in various conditions, C<sub>2</sub>H<sub>2</sub> and elemental sulfur, or CS<sub>2</sub>, were also detected. In a study performed in a wide range of temperatures (600–1000 °C), in a continuous flow experiment at atmospheric pressure, and in a current of argon with a residence time in the heated zone of 20s [63], a number of decomposition products were detected in the pyrolysate. These are shown in Table 21.3.1 as a function of decomposition temperature of thiophene.

The benzodithiophenes and benzotrithiophenes include several isomers such as benzo[1,2-*b*:3,4-*b'*]dithiophene, benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene, etc.

Pyrolysis of thiophene occurs by a free radical mechanism, starting with a C–H bond cleavage, as shown in the following reaction:

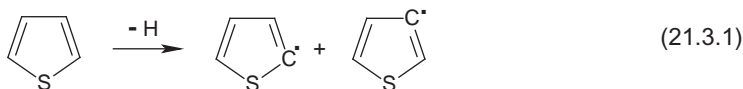


TABLE 21.3.1. *Percent of various compounds in the pyrolysis condensate of thiophene in a continuous flow experiment at different temperatures [63]*

No.	Compound Temperature (°C)	Composition (%)							
		600	700	750	800	850	900	950	1000
1	Thiophene	100	93.5	88.2	53.4	33.4	12.2	3.8	0
2	Carbon disulfide	0	0	0	4.0	4.0	24.1	33.8	57.4
3	Benzene	0	0	0	0	1.0	3.9	5.0	7.4
4	Naphthalene	0	0	0	0	1.6	9.1	15.0	9.8
5	Phenanthrene	0	0	0	0	0	4.2	4.8	2.4
6	Fluoranthene	0	0	0	0	0	1.7	2.9	2.2
7	Pyrene	0	0	0	0	0	1.2	2.6	3.1
8	2,3'-Dithiophene	0	6.0	11.1	36.9	18.7	1.2	2.7	3.3
9	Benzo[ <i>b</i> ]thiophene	0	0.3	0.7	7.3	25.6	28.6	16.9	5.1
10	Dibenzothiophene	0	0	0	0.9	6.6	10.7	9.6	6.3
11	Benzodithiophenes	0	0	0	0	1.4	0.8	0	0
12	Benzotrithiophenes	0	0	0	0	1.6	0	0	0
13	2-Phenylthiophene	0	0	0	0	2.2	0.8	0	0
14	Thianthrene	0	0	0	0.4	4.0	0	0	0
15	Terthiophene	0	0	0	0.7	0	0	0	0

The resulting free radicals undergo either decomposition to form H<sub>2</sub>S, CS<sub>2</sub>, alkyl type small free radicals, and reactive molecules such as acetylene and diacetylene, or condensation reactions with the formation of dithiophene, thianthrene, etc. Reaction of acetylene and other free radicals with thiophene easily explains the formation of benzothiophene and other similar compounds. Larger molecules such as fluoreno[1,9*a*,9-*b*,*c*]thiophene and triphenyleno[1,1*a*,1*b*,2-*b*,*c*,*c*]thiophene were also tentatively identified at low levels in the pyrolysate [63].

A study of thiophene decomposition was performed in a shock tube experiment in the temperature range 1598–2022 K and pressures between 2.5 bar and 3.44 bar of the compound diluted with argon. At these elevated temperatures, the main sulfur-containing decomposition products were H<sub>2</sub>S and ethanethiol, with lower levels of CS<sub>2</sub> (particularly in the higher temperature range). The hydrocarbon species detected in the pyrolysate included mainly C<sub>2</sub>H<sub>2</sub> and lower levels of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>4</sub>, C<sub>4</sub>H<sub>2</sub>, C<sub>4</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, and lower levels of several C<sub>5</sub> and C<sub>6</sub> species [64]. The study indicated the kinetics of the decomposition of thiophene to follow an Arrhenius equation of the form  $k \text{ (s}^{-1}\text{)} = 2.2 \times 10^{11} \exp[-270 \text{ (kJ)/}R\text{T}]$ .

Thermal decomposition of 1- and 2-methylthiophene at 800–825 °C was also reported in the literature [59].

### **Benzo[*b*]thiophene and dibenzothiophene**

Among the few studies performed on pyrolysis of benzo[*b*]thiophene can be listed one performed in gas phase for the analysis of decomposition kinetics of this compound [6], a study of decomposition in plasma [62], and a study performed in a continuous flow system. The plasma pyrolysis study indicated the formation of char, sulfur, toluene, and phenylacetylene. The continuous flow pyrolysis study was performed in the temperature range 500–1000 °C, at atmospheric pressure in a current of argon, and with a residence time of the parent compound in the heated zone of 20 s [63]. The study reported the variation with pyrolysis temperature of the level of a number of compounds in benzothiophene pyrolysate, which are shown in Table 21.3.2.

Pyrolysis of benzothiophene takes place similarly to that of thiophene by a radicalic mechanism. Some of the free radicals are decomposed into smaller fragments that can generate polycyclic aromatic hydrocarbons, and some of the condensed compounds with condensed thiophene and carbon aromatic rings. The pyrolysis also generated some char, not accounted for in Table 21.3.2. The evaluation of the composition of char generated at 800 °C indicated the presence of larger condensed molecules

TABLE 21.3.2. Percent of various compounds in the pyrolysis condensate of benzothiophene in a continuous flow experiment at different temperatures [63]

No.	Compound Temperature (°C)	Composition (%)*								
		500	600	700	750	800	850	900	950	1000
1	Benzo[b]thiophene	99.4	98.8	96.0	74.8	57.8	56.7	56.0	42.5	16.5
2	Carbon disulfide	0	0	0	0	0	0.3	1.2	3.1	19.9
3	Benzene	0	0	0	0	0.1	0.4	1.7	5.7	15.6
4	Biphenyl	0	0	0	0	0	0	0.4	1.6	2.0
5	Naphthalene	0.4	0.4	0.4	0.4	0.5	1.0	2.8	6.9	8.4
6	Fluorene	0	0	0	0	0	0.2	0.5	0.6	0.6
7	Anthracene	0	0	0	0	0	0.3	0.8	0.9	0
8	Phenanthrene	0	0	0	0	0.1	0.9	3.8	8.1	5.4
9	Fluoranthene	0	0	0	0	0.2	0.8	2.2	4.3	5.0
10	Pyrene	0	0	0	0	0	0.3	0.8	1.8	3.3
11	Benzo[k]fluoranthene	0	0	0	0	0	0	0.5	1.7	0
12	Methylbenzo[b]thiophene	0.3	0.6	0.4	0.5	0.3	0.6	0	0	0
13	3,3'-Di(benzo[b]thiophene)	0	0	3.2	23.6	35.8	14.4	2.6	0	0
14	3-Phenylbenzo[b]thiophene	0	0	0	0.3	0.4	2.3	2.6	0	0
15	Benzo[b]naphtho[2,1-d]-thiophene	0	0	0	0.1	2.4	12.9	11.1	5.1	0
16	[1]Benzothieno[2,3-b][1]-benzothiophene	0	0	0	0	0.1	3.1	5.2	1.4	0
17	Dibenzothiophene	0	0	0	0	0.1	0.9	3.5	10.6	16.2
18	Benzo[1,2-b:3,4-b']-dithiophene	0	0	0	0	0	1.0	0.8	0	0
19	Fluoreno[1,9a,9-b,c]-thiophene	0	0	0	0	0	0.6	2.4	5.8	7.7
20	Phenanthro[3,3a,4-b:5,5a,6-b']dithiophene	0	0	0	0	1.3	2.7	1.0	0	0

\*The percentage of some of the compounds listed included the levels of their isomers.

TABLE 21.3.3. Percent of various compounds in the pyrolysis condensate of dibenzothiophene in a continuous flow experiment at 900 °C [63]

No.	Compound	%
1	Dibenzothiophene	83.3
2	Benzo[1,2-b:4,5-b']bis[1]benzothiophene	8.9
3	4-Phenyldibenzothiophene	4.6
4	Triphenyleno[1,1a,1b,2-b,c,d]thiophene	2.1
5	Benzene	0.5
6	Biphenyl	0.4
7	Triphenylene	0.3

containing thiophene cycles, such as tentatively identified compounds: 3,3':2',3''-ter(benzo[b]thiophene), benzo[1,2-b:3,4-b':6,5-b'']tri(benzo[b]thiophene), tetra(benzo[b]thiophenes), penta(benzo[b]thiophenes), and even hexa(benzo[b]thiophenes).

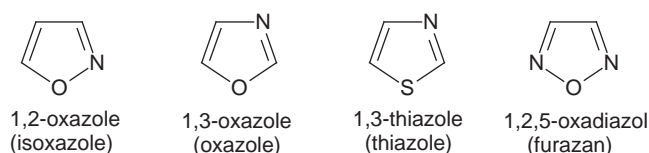
Studies on dibenzothiophene pyrolysis showed that the compound is very stable to heating [6,63,65]. In a continuous flow pyrolysis study performed at 900 °C with 20 s heating time [63], the reported composition of pyrolysate (not including char) is that shown in Table 21.3.3.

A different experiment was conducted at lower temperatures in the range 375–500 °C but with heating time between 1 hour and 2 months [66]. The compounds identified in the pyrolysates included, besides undecomposed dibenzothiophene, compounds such as H<sub>2</sub>S, benzothiophene dimers, phenyldibenzothiophene, benzo-bis-benzothiophene, and compounds that have no sulfur in their composition such as H<sub>2</sub>, CH<sub>4</sub>, biphenyl, and benzene.

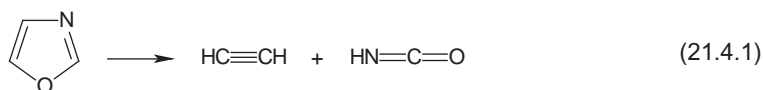
## 21.4. AROMATIC HETEROCYCLES CONTAINING DIFFERENT HETEROATOMS

### General aspects

Heterocyclic aromatic compounds can contain in their molecule, besides carbon, two or more different heteroatoms. A few examples of such heterocycles with five-atom rings are shown below:

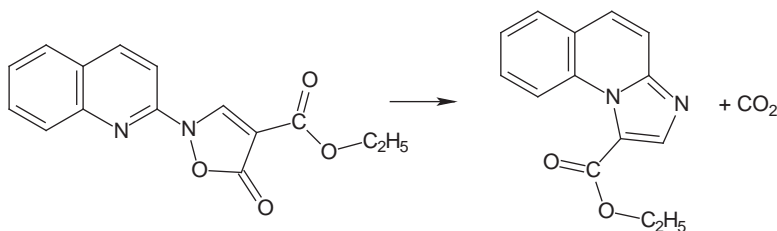


These heterocycles are typically stable to heating. Oxazole, for example, decomposes at temperatures exceeding 600 °C by the following reaction:



Isocyanic acid further generates the typical trimer (cyanuric acid). Other condensation products can be generated in the pyrolysate [67].

Although studies on the pyrolysis of simple heterocycles with different atoms in the molecule is not abundant in the literature, various results are published regarding derivatives of these compounds when other functional groups are present in the molecule [68–73,15]. The presence of specific substituents may influence the reaction outcome, as shown as an example in the following reaction:



Thermal properties of some compounds with specific functionalities were of particular interest since they have utilization that may involve heating. This is, for example, the case for furazans substituted with nitro (NO<sub>2</sub>), amino (NH<sub>2</sub>), or nitramino (NHNO<sub>2</sub>) groups that are used as energetic materials [74]. During thermal decomposition of nitro or nitramino furazan, the furazan ring is opened, generating cyanogens-N-oxide (NC–CNO) followed by other reactions involving the substituents.

When pyrolysis is done in flash mode at temperatures up to 800–900 °C, the heterocycles in complex molecules containing stable moieties such as oxazole or thiazole tend to maintain their integrity (not the case of furazan cycle). The cleavage of other bonds in the molecule is usually the first to occur. An example is given for the pyrolysis of sulfathiazole or 4-amino-*N*-(1,3-thiazol-2-yl)benzenesulfonamide, which was performed in a Type 1 Experiment as described in Section 4.6, at  $T_{\text{eq}} = 900$  °C,  $\beta = 10$  °C/ms, THT = 10 s, and housing temperature  $T_{\text{hou}} = 280$  °C. The analysis of pyrolysate was done



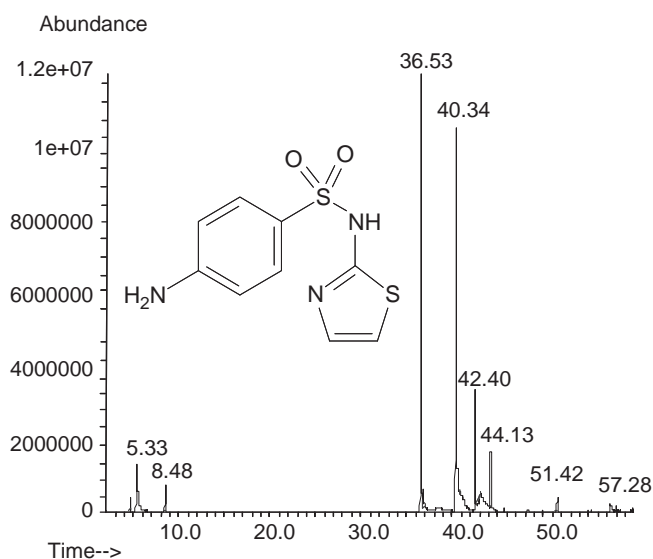


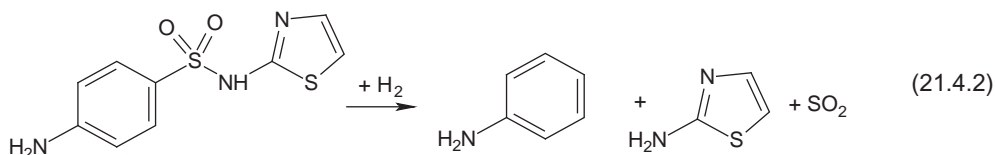
FIGURE 21.4.1. Pyrogram obtained at 900°C for sulfathiazole CAS no. 72-14-0 (MW = 255).

TABLE 21.4.1. Identification of the main peaks in the chromatogram shown in Figure 21.4.1 for the pyrolysis of sulfathiazole at 900°C ( $H_2$ ,  $H_2O$ ,  $HCN$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ ,  $N_2$  not included due to the MS settings)

No.	Compound	Ret. time (min)	MW	CAS no.	Mole percent
1	Hydrogen sulfide	4.63	34	7783-06-4	0.58
2	Carbonyl sulfide	4.69	60	463-58-1	0.05
3	Sulfur dioxide	5.33	64	7446-09-5	<b>7.48</b>
4	Carbon disulfide	8.48	76	75-15-0	1.02
5	Aniline	36.53	93	62-53-3	<b>68.10</b>
6	Benzonitrile	36.81	103	100-47-0	0.74
7	2-Amino-1,3-thiazole	40.35	100	96-50-4	<b>18.11</b>
8	Benzene isothiocyanate	42.40	135	103-72-0	2.13
9	Benzothiazole	44.13	135	95-16-9	1.15
10	2-Cyanobenzothiazole	51.42	160	N/A	0.37
11	2-Benzothiazoleamine	57.28	150	136-95-8	0.24
12	2(3H)-Benzothiazolone	60.43	151	934-34-9	0.02

exclusively by GC/MS under conditions given in Table 4.6.1. The pyrogram is shown in Figure 21.4.1, and the list of identified compounds is given in Table 21.4.1.

As shown in Table 21.4.1, the main pyrolysis products of sulfathiazole are aniline and 2-amino-1,3-thiazole resulting by the following reaction:



Reaction 21.4.2 requires a source of hydrogen generated from some other simultaneous reactions including char formation.

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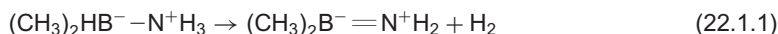
## CHAPTER 22

*Pyrolysis of Other Compounds with Heteroatoms***22.1. BORON-CONTAINING COMPOUNDS****General aspects**

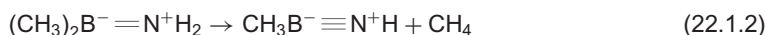
Boron can form compounds with the formula  $BR_3$ , where R is an alkyl or aryl radical. Thermal decomposition of such compounds has been reported in relation to the deposition of boron on surfaces such as silicon for doping purposes in electronic industry [1]. One example is the decomposition of trimethylborane,  $B(CH_3)_3$ , which takes place at temperatures above  $900^\circ\text{C}$  or in glow discharge systems and has been used for making highly boron-doped P-type silicon nanowires [2]. The compound has a B–C bond dissociation energy of about 87 kcal/mol, and its thermal decomposition takes place by a sequential loss of methyl groups.

Boron-doped graphite can be obtained by the thermal decomposition of triphenylboron vapors at  $800^\circ\text{C}$ , which generates films with the composition  $C_{16-18}B$  [3]. Triphenylboron reacts with phenylmagnesium bromide after treatment with NaCl to produce sodium tetraphenylborate, a compound with the formula  $(C_6H_5)_4B^-Na^+$ . Thermal decomposition of this compound leads to the formation of a mixture of aromatic hydrocarbons [4,5].

Organic compounds of boron have the capability to react with ammonia and amines to form borazanes  $R_3B^- - N^+R_3^b$  ( $R^a, R^b = H, \text{alkyl, etc.}$ ). These compounds by thermal decomposition around  $150^\circ\text{C}$  generate borazenes [6], as shown in the following reaction:



Further pyrolysis of borazenes at temperatures around  $250^\circ\text{C}$  generate borazynes.



Borazynes have the tendency to polymerize to form trimers known as borazines or borazoles, which have a stable six-atom ring cycle.

Thermal decomposition of boric acid esters,  $B(OR)_3$ , has been discussed in Section 19.2.

**22.2. SILICON-CONTAINING COMPOUNDS****General aspects**

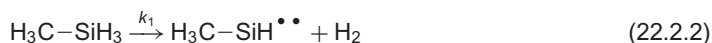
Although silicon and carbon are elements of the same group in the periodic table, and they would be expected to form similar compounds, silicon compounds show considerable differences from those of carbon. The Si–Si bond average energy is 52 kcal/mol, which is about 30 kcal/mol weaker than the C–C bond, which has an average energy of about 83 kcal/mol. The energy for Si–H bond is around 75 kcal/mol, as compared to C–H bond with 99 kcal/mol. Also, silicon does not form stable multiple bonds with itself or other elements. However, the C–Si bond has the energy of 76 kcal/mol, and silicon can form alkylated or arylated compounds analogous with regular hydrocarbons. Also, functional groups such as halogen,  $-OH$ ,  $-O-$ , or amino can be directly bound to the silicon atom. These possibilities lead to a large variety of organic compounds that have one or more carbon atoms replaced by a silicon atom.

Silane,  $SiH_4$ , is methane equivalent in the series of chemical combinations of carbon but is not an organic compound. Methylsilane,  $CH_3-SiH_3$ , pyrolysis has been studied mainly related to the deposition

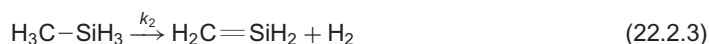
of silicon carbide, SiC [7–9]. The main decomposition reaction of  $\text{CH}_3\text{-SiH}_3$  can be written as follows:



This reaction starts with a 1,1-hydrogen elimination to form methyilsilylene [10].



Two other reactions are associated with this process, a 1,2-hydrogen elimination and a reaction with the formation of methane:



Molecules such as  $\text{CH}_3\text{-SiH}^{\bullet\bullet}$ ,  $\text{CH}_2\text{=SiH}_2$ , and  $\text{SiH}_2^{\bullet\bullet}$  are not stable and cannot be isolated, continuing a fast decomposition process with the formation of SiC. The  $\text{H}_2$  elimination at 700 K represents about 94% of the process (with about 78% from reaction 22.2.2 and 16% from reaction 22.2.3) and that of  $\text{CH}_4$  formation about 6% [11,12]. At higher temperatures (1125–1250 K) the efficiency of  $\text{H}_2$  elimination is about 91%. The decomposition of  $\text{CH}_3\text{-SiH}_3$  is also associated with the formation of small levels of  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{SiH}_2(\text{CH}_3)_2$ , and  $\text{SiH}_4$ . The decrease in mole fraction of  $\text{CH}_3\text{-SiH}_3$  as a function of temperature at 0.1 s exposure time is shown in Figure 22.2.1.

The study of kinetic parameters for reactions 22.2.2–22.2.4 indicated that Arrhenius equations for the processes have the expressions:  $(k_1+k_2) (\text{s}^{-1}) = 10^{15.2} \exp[-64.78 (\text{kcal})/RT]$ , and  $k_3 (\text{s}^{-1}) = 10^{14.5} \exp[-67.6 (\text{kcal})/RT]$ . Similar parameters were obtained for deuterated methylsilane,  $\text{CH}_3\text{-SiD}_3$  [13].

The decomposition of  $\text{CH}_3\text{-SiH}_3$ , depending on the temperature, pressure, and the nature of heterogeneous reactions, generates films with specific Si/C/H compositions. Similar decomposition reactions with methylsilane are given by other compounds such as  $(\text{CH}_3)_2\text{SiH}_2$ ,  $(\text{CH}_3)_3\text{SiH}$ ,  $\text{H}_2\text{C=CH-SiH}_3$ ,  $\text{HC}\equiv\text{C-SiH}_3$ , or by halogenated methylsilanes [9,14]. Some studies were performed on these compounds with the purpose to generate films with Si/C/H ratios as low as possible in hydrogen. Pyrolysis of prop-2-enylsilane generates SiC and also  $\text{C}_2\text{H}_4$ ,  $\text{CH}_3\text{SiH}_3$ , propene, and several  $\text{C}_3\text{H}_4$  hydrocarbons [14]. The almost pure SiC was generated by the decomposition of ethynylsilane, which also forms  $\text{C}_2\text{H}_2$  and some  $\text{CH}_4$ ,  $\text{SiH}_4$ , and  $\text{C}_2\text{H}_4$ .

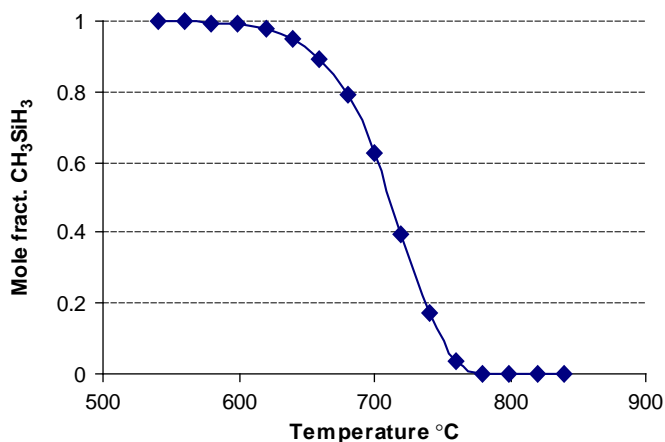


FIGURE 22.2.1. Mole fraction of  $\text{CH}_3\text{-SiH}_3$  as a function of temperature at 0.1 s exposure time.

Other studies on organosilicon compounds were performed on tetraphenylsilane, which is stable up to about 530 °C, on bis(alkoxyethynyl)-substituted silanes with the general formula  $(\text{H}_3\text{C})\text{RSi}(\text{C}\equiv\text{COR}')_2$ , with  $\text{R}=\text{H}$  or  $\text{CH}_3$ , and  $\text{R}'=\text{CH}_3$  or  $\text{C}_2\text{H}_5$  [15], etc.

Pyrolysis results were also reported for allyltrimethylsilanes, where two concurrent reactions take place in the process, one being homolysis of the silicon-allyl bond and the other a retro-ene elimination of dimethylsilene [16]. Also, pyrolysis of 4-(dimethylsilyl)-1-butene, 4-(trimethylsilyl)-1-butene, 5-(dimethylsilyl)-1-pentene, and 5-(trimethylsilyl)-1-pentene has been reported [16].

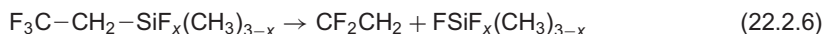
Compounds with a Si–Si bond were studied regarding their decomposition around 600 °C. Hexamethyldisilane decomposes mainly with the formation of trimethylsilane and trimethyl(dimethylsilylmethyl)silane [17]. The reaction mechanism starts with the Si–Si cleavage as shown in the reactions listed in Table 22.2.1. Similar reactions to those from Table 22.2.1 were described for the photolysis of other compounds with Si–Si bonds.

Regarding halogenated silanes, most studies were performed on trichloromethylsilane. The main decomposition of this compound is described by the following reaction:



Pyrolysis of trichloromethylsilane was studied experimentally and theoretically in a wide range of temperatures, and a set of 114 reactions was generated to explain the deposition of SiC from this compound decomposition [18,19].

Other halogenated silanes evaluated regarding their thermal decomposition include several fluorinated compounds. Their list is given in Table 22.2.2, together with the Arrhenius parameters for the decomposition reaction that generates mainly  $\text{CF}_2=\text{CH}_2$  and is shown below ( $x = 0, 1, 2, 3$ ) [20]:



Pyrolysis of several compounds containing Si–O bonds were evaluated and reported in the literature (see also Section 16.3). In one such study, attempts were made to generate a compound containing a Si=C bond [21]. The formation of olefins easily takes place during the decomposition of esters with hydrogens at the  $\beta$ -carbon of the alcohol (see Section 19.1). For example, a tertiary phthalate ester generates by thermal decomposition at low temperatures (150–200 °C) an olefin and phthalic anhydride

TABLE 22.2.1. Typical reactions in the decomposition of hexamethyldisilane [17]

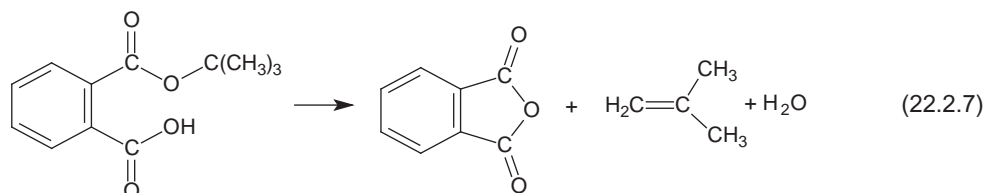
Reaction
Initiation reaction
$(\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_3 \rightarrow 2(\text{CH}_3)_3\text{Si}^\bullet$
Propagation reactions
$(\text{CH}_3)_3\text{Si}^\bullet + (\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_3 \rightarrow \textbf{(\text{CH}_3)_3\text{SiH}} + (\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_2\text{CH}_2^\bullet$
$(\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_2\text{CH}_2^\bullet \rightarrow \bullet\text{Si}(\text{CH}_3)_2-\text{CH}_2-\text{Si}(\text{CH}_3)_3$
$\bullet\text{Si}(\text{CH}_3)_2\text{CH}_2-\text{Si}(\text{CH}_3)_3 + (\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_3 \rightarrow \textbf{(\text{CH}_3)_3\text{Si}-CH}_2\textbf{-Si}(\text{CH}_3)_3 + (\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_2\text{CH}_2^\bullet$
Termination reaction
$2(\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_2\text{CH}_2^\bullet \rightarrow (\text{CH}_3)_3\text{Si}-\text{Si}(\text{CH}_3)_2-\text{CH}_2-\text{CH}_2-(\text{CH}_3)_2\text{Si}-\text{Si}(\text{CH}_3)_3$

Note: Bold letters indicate the main reaction products.

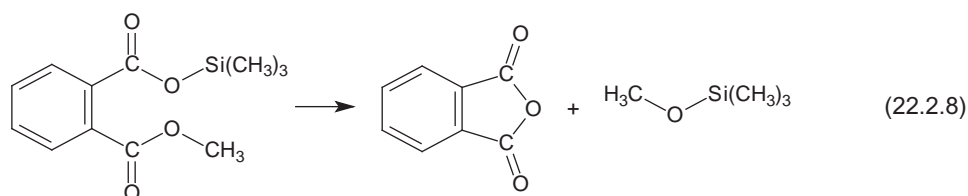
TABLE 22.2.2. Arrhenius parameters for reaction 22.2.6 applied to several fluorinated silanes [20]

Compound	A	$E^\ddagger$ (kcal/mol)
$\text{CF}_3\text{CH}_2\text{Si}(\text{CH}_3)_3$	$2.40 \times 10^{12}$	47.24
$\text{CF}_3\text{CH}_2\text{SiF}(\text{CH}_3)_2$	$3.89 \times 10^{12}$	41.35
$\text{CF}_3\text{CH}_2\text{SiF}_2(\text{CH}_3)$	$3.89 \times 10^{12}$	39.57
$\text{CF}_3\text{CH}_2\text{SiF}_3$	$3.16 \times 10^{12}$	37.01

as shown in the reaction below:



A similar reaction was attempted for several silanol esters such as methyldiphenylsilyl, trimethylsilyl, and benzyldiphenylsilyl methyl phthalate [21]. The result of pyrolysis of these esters at 400–470 °C was the formation of alkoxy silanes and not a silylene, as shown in the following reaction for trimethylsilyl methyl phthalate:



Trimethylsilyl 2-octyl phthalate generated in the same reaction 1-(1-methylheptyloxy)-trimethylsilane [21].

Among the studies on chlorinated siloxanes, pyrolysis of 1,1,1-trimethyl-3,3,3-trichlorodisiloxane was reported [22]. Pyrolysis of this compound at 650 °C generates a mixture of compounds including trimethylchlorosilane, 1,1,1,3,3-pentamethyl-5,5,5-trichloro-trisiloxane, 1,1,1-trimethyl-3,3,5,5,5-penta-chlorotrisiloxane, trichloromethylsilane, and 1,1,1,3,3-pentamethyl-3-chlorodisiloxane. The reaction is assumed to have a radicalic mechanism.

Other pyrolysis results are reported for organosilicon peroxides [23], pyrolysis of phenylsilaisocyanide, which generates a compound with a  $\text{Si}\equiv\text{N}$  bond [24], on silazanes [25], and on heterocyclic compounds containing Si atoms in the ring [26]. Information on the formation by pyrolysis and stability of cyclotrisiloxanes, cyclotetrasiloxanes, cyclopentasiloxanes, etc., with different substituents such as  $\text{CH}_3$  or  $\text{C}_6\text{H}_5$  on the ring are also available in the literature [27].

## 22.3. PHOSPHORUS AND ARSENIC-CONTAINING COMPOUNDS

### *Organic compounds of phosphorus*

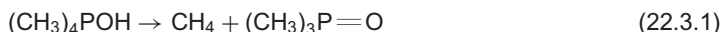
Since phosphorus and nitrogen are in the same group of the periodic table, some similarities between the combinations of these two elements would be expected. However, phosphorus is more electropositive than nitrogen and forms with the halogens and oxygen more stable combinations. On the other hand, the compounds with hydrogen are less stable. The use of d-orbitals allows phosphorus to exist in some compounds with five covalent bonds. The end result is that differences are seen between the combinations of nitrogen and phosphorus.

Due to the more electropositive character of phosphorus compared to nitrogen, primary and secondary phosphines are not very stable to pyrolysis. Pyrolysis of several phosphines ( $\text{PR}_3$ ,  $\text{R}=\text{H}$ , alkyl, aryl) has been performed with the purpose of making phosphorus-doped materials with metals such as Ga or In necessary in electronic industry [28,29]. The decompositions take place with free radical mechanisms leading to the formation of hydrocarbons and releasing phosphorus that typically forms a combination with a metal simultaneously deposited to form an epitaxial film. For tertiary butylphosphine, for example, the main pyrolysis products include the metal phosphide GaP when pyrolysis is performed in the presence of trimethyl gallium,  $\text{H}_2$ , and butene (InP can be generated in a similar manner).

Pyrolysis of pure phosphines has been reported for diallylphenyl, allylbenzylphenyl, and allylmethylphenyl phosphines. These compounds were pyrolyzed in a stirred-flow reactor at 380–429 °C and 7–20 Torr with toluene as carrier gas. The main reaction products were propene, 1-phospha-1,3-butadiene, 1-phospha-1,2-diphenylethylene, and 1-phosphaethylene. The phospha-alkenes that were formed transformed into cyclo addition products. A six-center cyclic transition state unimolecular reaction mechanism was proposed for the propene elimination reaction. The propene elimination reaction showed first-order kinetics with rate coefficients having the Arrhenius equations as follows [30]:

for diallylphenylphosphine  $k \text{ (s}^{-1}\text{)} = 10^{10.57 \pm 0.31} \exp[-143 \pm 4 \text{ (kJ/mol)/}RT]$ ,  
 for allylbenzylphenylphosphine  $k \text{ (s}^{-1}\text{)} = 10^{9.71 \pm 0.47} \exp[-135 \pm 6 \text{ (kJ/mol)/}RT]$ , and  
 for allylmethylphenylphosphine  $k \text{ (s}^{-1}\text{)} = 10^{9.61 \pm 0.61} \exp[-144 \pm 9 \text{ (kJ/mol)/}RT]$ .

Similar to ammonia and amines, phosphines can form hydroxides and salts  $[\text{PR}_4]^+\text{X}^-$ , where  $\text{R} = \text{H}$ , alkyl, aryl, acyl, and  $\text{X} = \text{OH}$ , halogen, etc. Tetramethylphosphonium hydroxide decomposes when heated as shown in the following reaction:

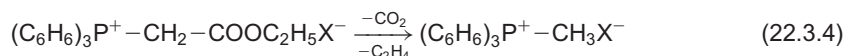
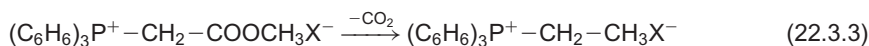


Tetraethylphosphonium hydroxide decomposes similarly. Tetraethylphosphonium acetate generates a mixture of triethylphosphine, triethylphosphine oxide,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and ethyl methyl ketone. Other organic salts generate a similar mixture by pyrolysis [31]. Tetramethylphosphonium chloride pyrolyzes generating trimethylphosphine, as shown in the following reaction:



In the case of different substituents at the phosphorus atom, the detached group during pyrolysis depends on the anion, and it is different for the hydroxide as compared to chloride. In the case of hydroxide, the phenyl group is readily detached and the alkyl groups are more strongly attached, while for the chloride the order is reversed.

Thermal decomposition of a number of triphenylphosphonium alkyl ester salts was also reported in the literature [32]. These compounds decompose at temperatures between 130 °C and 225 °C to generate a mixture of compounds by  $\text{CO}_2$  elimination and formation of an ylide, which further interacts with other pyrolysis products. The main reactions are shown below for the phosphonium methyl and ethyl salts:



Other pyrolysis products include  $(\text{C}_6\text{H}_5)_3\text{P}=\text{O}$ , dimers and trimers of the parent compound, etc.

Phosphines have a strong donor character and form complexes with transitional metal salts. Thermal decomposition of several such compounds is reported in the literature [33–36].

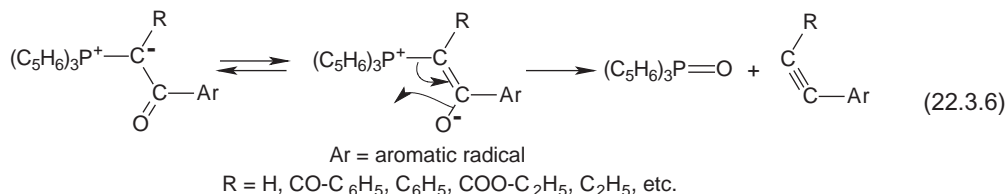
Other compounds related to phosphine include phosphine oxides  $\text{R}_3\text{P}=\text{O}$ , phosphazenes  $\text{R}_2\text{C}=\text{N}-\text{N}=\text{PR}_3$ , and phosphine–borane complexes  $\text{R}_3\text{P} \rightarrow \text{BH}_3$ , where  $\text{R}$  are alkyl or aryl radicals. Pyrolysis of such compounds has also been reported [37,38]. Phosphazenes, for example, generate by pyrolysis diazo compounds and phosphines by the following reaction:



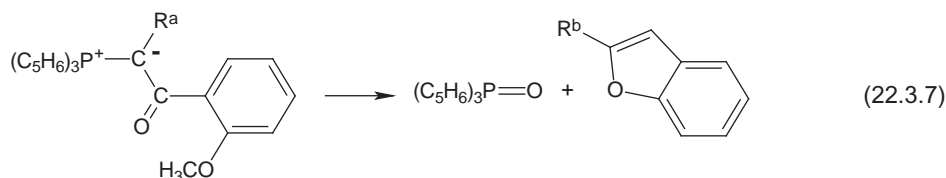
Phenylphosphine–borane complex, for example, heated around 150 °C generates  $\text{H}_2$  and changes into a polymeric material. At temperatures around 250 °C, phenylphosphine is generated, leaving a polymeric residue.



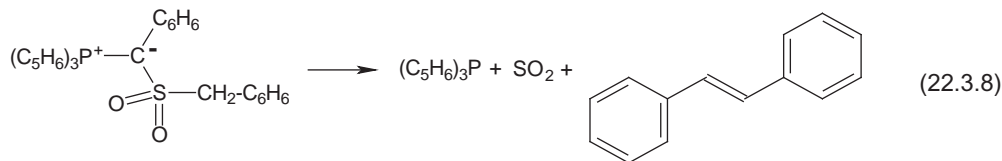
A considerable amount of information is available regarding the pyrolysis of phosphonium ylides [39–46]. Ylides are neutral molecules with a positive and a negative charge on adjacent atoms, phosphonium ylides being probably the most common ones. A typical ylide is a phosphonium ylide with the formula  $(\text{C}_6\text{H}_5)_3\text{P}^+-\text{CR}_2^-$ , which can be written in the triphenylphosphorane form  $(\text{C}_6\text{H}_5)_3\text{P}=\text{CR}_2$ . Stabilized ylides, when heated around  $700^\circ\text{C}$ , undergo the following type of reaction:



At higher temperatures and depending on the R and Ar radicals (including heterocycles) [47], a different reaction path is possible, as shown below for the decomposition at  $850^\circ\text{C}$  of an ylide with Ar an o-methoxyphenyl radical [48]:



For  $\text{R}^a = \text{CH}_3$ , the resulting pyrolysate is a mixture of  $\text{R}^b = \text{CH}_3$  and  $\text{R}^b = \text{C}_2\text{H}_5$ . Stabilized sulfinyl phosphonium ylides and sulfonyl phosphonium ylides were also studied. Various reactions were possible during pyrolysis of these compounds. Some of these sulfinyl [49] or sulfonyl triphenylphosphoranes eliminate  $(\text{C}_6\text{H}_5)_3\text{P}=\text{O}$ , but other reactions are also possible. One such example is shown below for [(phenylmethylsulfonyl)(phenyl)methylene]triphenylphosphorane [50]:



Other reaction products, at lower levels, are also generated in reaction 22.3.8, including  $(\text{C}_6\text{H}_5)_3\text{P}=\text{O}$ ,  $(\text{C}_6\text{H}_5)_3\text{P}=\text{S}$ , etc.

Some kinetic parameters are reported for ylide pyrolysis [51]. Pyrolysis of other compounds containing phosphorus was reported in the literature (see also Section 19.2).

### Organic compounds of arsenic

Arsenic is in the same group of the periodic table with nitrogen and phosphorus, but its electropositive character is even stronger than that of phosphorus (which is stronger than that of nitrogen). For this reason, arsenic combinations with hydrogen, as well as primary and secondary arsines, are not very stable. Arsenic is more stable in the valence state of five.

Primary and secondary arsines generate by pyrolysis around  $300^\circ\text{C}$  arsenic (metallic), hydrocarbons, and depending on the substituent some trialkyl arsines. The reactions can be written as follows:



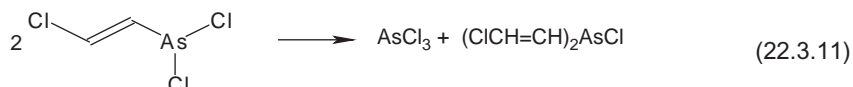
Methyl arsine decomposes mainly by reaction 22.3.9, while ethyl arsine decomposes by both reactions 22.3.9 and 22.3.10. An exception is benzyl arsine which by pyrolysis generates  $H_2$  and a polymeric material.

Trialkyl and triaryl arsines generate arsenic and hydrocarbons by pyrolysis at slightly higher temperatures than  $300^\circ C$ . For example, triphenylarsine generates As and biphenyl, and also other decomposition products including char.

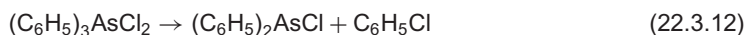
Arsenic has the capability to form diarsines (e.g., tetramethyldiarsine or cacodyl, tetraphenyldiarsine, etc.). Tetraphenyldiarsine generates by heating triphenylarsine and As, while cacodyl generates trimethylarsine and a polymeric methyl arsine.

Quaternary hydroxides and salts of As are stable, and the compounds with the formula  $R_4AsOH$  are strong bases. Depending on the R radical, these compounds decompose generating the corresponding arsine and the alcohol ROH, and also other decomposition products. Arsine dihydroxides,  $R_3As(OH)_2$ , are known compounds that change into  $R_3As=O$  and water by decomposition at around  $100^\circ C$ . Arsine oxides further decompose upon heating to generate  $As_2O_3$  and arsines. Arsenic also forms arsine sulfides and arsine disulfides. Phenyl arsine sulfide decomposes to generate  $As_2S_3$  and triphenylarsine [31].

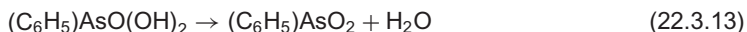
Arsenic forms strong bonds with halogens (compared to phosphorus and nitrogen). Some of the partly chlorinated derivatives by pyrolysis tend to suffer disproportionation reactions as shown for  $\beta$ -chlorovinyl dichloro arsine (Lewisite) [52]:



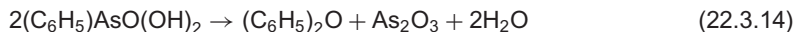
Halogenated compounds of As in valence five may decompose with the formation of combinations of As in valence three, as shown in the following reaction:



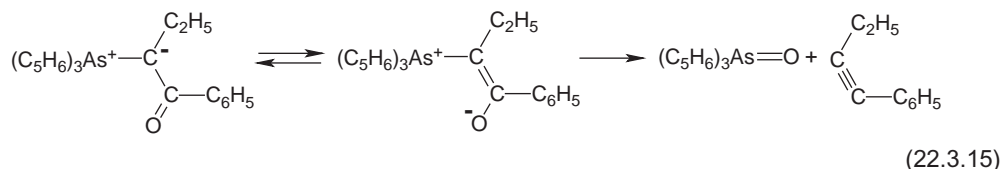
Phenylarsonic acid heated around  $140^\circ C$  loses water by the following reaction:



Pyrolyzed at  $320^\circ C$ , phenylarsonic acid decomposes to form diphenylether,  $As_2O_3$ , and  $H_2O$  as shown in the following reaction:



Similar to phosphorus, arsenic forms arsonium ylides. The decomposition of these compounds takes place in similar manner as for the phosphonium ylides, as shown in the following reaction [51]:



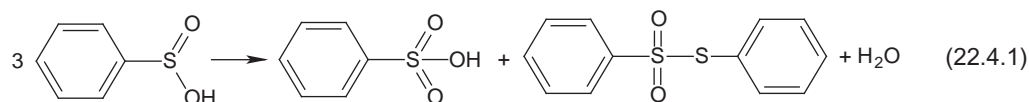
Antimony (Sb) is an element even more electropositive than arsenic. The properties of antimony organic compounds resemble those of arsenic, with even more tendency to form bonds with oxygen and halogens and lower stability of its bonds with hydrogen and carbon.

## 22.4. SULFUR-CONTAINING COMPOUNDS

### General aspects

Sulfur can participate in many organic combinations to produce compounds such as thiols, sulfides, disulfides, thioaldehydes, thioketones, thioacids, thioesters, thioamides, thiourea derivatives, or heterocycles such as thiophene. Pyrolysis of these types of compounds was previously presented in dedicated chapters or sections of this book (see, e.g., Chapter 12, Section 15.4, Section 17.6, Section 19.10, part of Chapter 20, Section 21.3). However, sulfinic acids ( $R-SO_2H$ ), sulfonic acids ( $R-SO_3H$ ), sulfoxides ( $R_2SO$ ), sulfones ( $R_2SO_2$ ), and some of their related compounds were not captured in previous discussions.

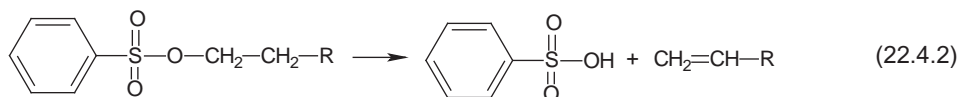
Sulfinic acids typically undergo an oxido-reduction reaction upon heating at temperatures around  $150^\circ\text{C}$ . For example, benzene sulfinic acid,  $C_6H_5SO_2H$ , changes into a mixture of sulfonic acids and benzenesulfothioic acid S-phenyl ester.



As temperature increases, the reaction products continue the decomposition process, generating a complex mixture.

Sulfonic acids usually decompose at higher temperatures compared to the corresponding carboxylic acids. For example, dibromosulfoacetic acid decomposes to form  $\text{CO}_2$  and dibromomethyl sulfonic acid [31]. Benzenesulfonic acid by itself starts decomposing at temperatures above  $300^\circ\text{C}$  to generate a mixture of compounds containing benzene, biphenyl, diphenylsulfide, thiophenol,  $\text{SO}_3$ ,  $\text{SO}_2$ , etc. A similar reaction is given by the ammonium salt of benzenesulfonic acid, which in addition generates some benzensulfonamide.

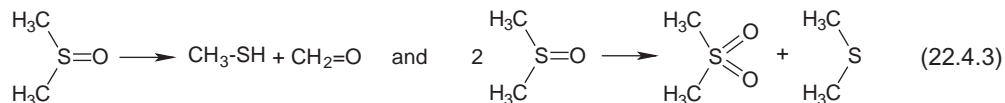
The esters of sulfonic acids are typically more stable to heating as compared to the corresponding carboxylic acid esters. Pyrolysis of the esters of sulfonic acids takes place similarly to that of sulfuric acid esters (thermal decomposition of sulfuric acid esters was presented in Section 19.2). When the alcohol group has an available  $\beta$ -hydrogen, the reaction takes place with the formation of alkenes as shown in the following example:



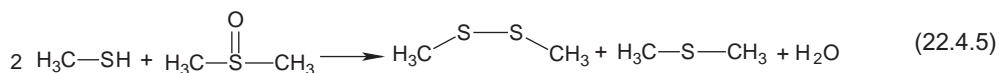
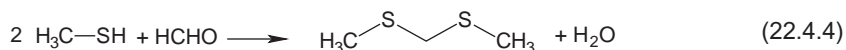
Common derivatives of sulfonic acids are sulfonamides where the OH group from a sulfonic acid is replaced by  $\text{NH}_2$ , a primary, or a secondary amine. An important class of antimicrobial agents is that of sulfonamides (sulfa drugs). The decomposition of sulfonamides typically takes place with elimination of  $\text{SO}_2$  and formation of fragments from the two sides of the sulfone group. For example, pyrolysis of sulfanilamide,  $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{SO}_2\text{NH}_2$ , generates  $\text{SO}_2$  and aniline as the main reaction products, with traces of *N*-sulfinyl-benzeneamine and 2,1,3-benzothiadiazole ( $\text{N}_2$  and  $\text{NH}_3$  not analyzed). Char is also generated during pyrolysis. Pyrolysis of a number of sulfa drugs was reported in the literature [53,54], particularly with the purpose of analysis. The structure of the substituent at the amino group is typically more diagnostic for the sulfa drug identification. One example of pyrolysis of a sulfonamide was given in Section 21.4 for sulfathiazole.

Sulfoxides are relatively stable compounds to heating. Dimethylsulfoxide,  $(\text{CH}_3)_2\text{S}=\text{O}$ , decomposes at temperatures above  $350^\circ\text{C}$  by two main reactions: elimination of  $\text{CH}_2\text{O}$  plus methylthiol

formation, and a disproportionation. These two reactions are shown below:

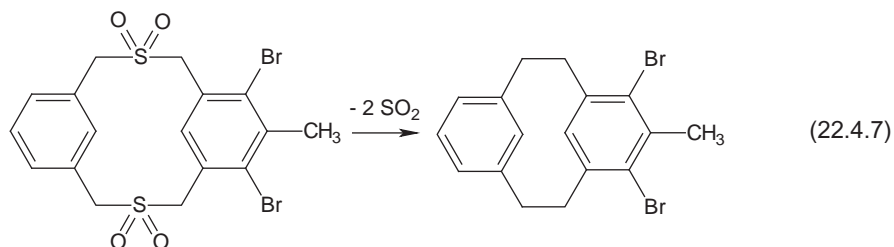
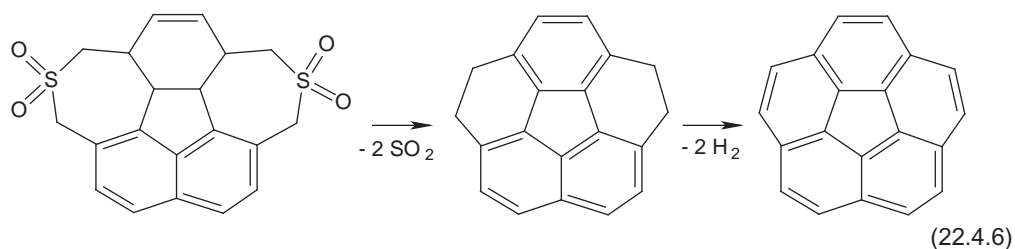


Formaldehyde and dimethylsulfide generated in reaction 22.4.3 further react to form bis-(methylthio)methane and water. Also, methylthiol reacts with excess dimethylsulfoxide to form dimethylsulfide and dimethyldisulfide. The reactions are shown below:



The end pyrolysate contains a mixture of formaldehyde (mainly as paraformaldehyde), dimethylsulfide, dimethyldisulfide, bis-(methylthio)methane, water, and some dimethylsulfone. Thermal decomposition of di-*tert*-butyl sulfoxide is also reported in the literature [55].

Sulfones by pyrolysis typically eliminate  $\text{SO}_2$  and, depending on the structure of the compound, may fragment or form new C-C bonds. For example, pyrolysis of divinylsulfone at 580–600 °C generates  $\text{SO}_2$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_2\text{H}_4$ , with lower levels of butadiene, benzene, toluene, xylenes, styrene, and benzothiophene [56]. Pyrolysis of cyclic sulfones, in particular, leads to the formation of new C-C bonds. This reaction has been used extensively for macrocycles synthesis [57–59], and for the synthesis of circulenes and cage compounds [60]. Two examples of  $\text{SO}_2$  elimination are shown below:



The benzyl moiety usually acts as an activating group for the  $\text{SO}_2$  elimination, although non-benzylic sulfone pyrolysis can also lead to new C-C bonds formation [61].

Pyrolysis of several sulfonium ylides was also reported in the literature [62].

## 22.5. ORGANOMETALLIC MOLECULES AND COMPOUNDS OF OTHER ELEMENTS

### General aspects

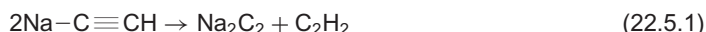
Various studies were performed on pyrolysis of organometallic compounds (see, e.g., [31,63,64]). However, there is a large variety of molecules that can be considered organometallic, and a systematic discussion regarding their thermal decomposition is not simple. Organometallic compounds can be classified in three general groups:

1. The compounds of metals from principal groups of the periodic table of elements, including compounds of Li, Na, K, Be, Mg, Ca, Ba, Al, Ga, In, Tl, Ge, Sn, Pb, etc. These compounds are stable to thermal decomposition.
2. The compounds of transition metals, which are less stable, except for the compounds of Zn, Cd, and Hg that have stability similar to those from the principal groups.
3. Complex compounds in which the  $\pi$ -electrons of alkenes or arenes form bonds with the d-electrons of specific metals.

A large number of molecules containing metal ions bound to an organic compound through ionic and coordinate bonds are possible. Studies on thermal stability of these molecules are available in the literature (see, e.g., [65–70]). Although these compounds were briefly discussed in Section 17.5 and other places, the subject is basically outside the purpose of this book.

### Organometallic compounds from the principal groups of elements

Alkyl derivatives of alkaline metals are stable compounds, and upon heating at temperatures above 350 °C, some of these compounds generate hydrocarbons and metal hydrides. Among the compounds for which pyrolysis results are reported, are acetylene derivatives [71]. The hydrogen in the acetylene molecule has a slight acidic character and can be replaced with Na, Ca, and also with transitional metals such as Cu(I) and Ag. Monosodium derivative of acetylene decomposes around 220 °C as shown below:



Sodium carbide,  $\text{Na}_2\text{C}_2$ , is very stable and decomposes only above 800 °C to form carbon and sodium. Very stable to heating are other carbides such as  $\text{CaC}_2$ , which also decomposes into elements at elevated temperatures. Other carbides can form upon heating subcarbides (e.g., magnesium forms a  $\text{Mg}_2\text{C}_3$  compound), which also decompose into elements at temperatures above 800–900 °C. Carbides of Ag and Cu(I) are less stable and decompose with explosion upon heating.

Organometallic compounds of alkali metals with the metal bound to an element other than carbon are also possible. For example, cesium forms a methanide with the formula  $\text{CH}_3\text{MgCs}$ . The decomposition of this compound takes place around 120 °C with the formation of  $\text{CsCN}$  and  $\text{H}_2$ . Lithium diisopropylamide (LDA), which is used in organic synthesis, is pyrophoric and not stable. Effort has been made to obtain LDA in a more stable form [72].

Pyrolysis of several organomagnesium compounds of the form  $\text{RMg}^+\text{X}^-$  takes place at lower temperatures with the formation of alkenes, metal hydrides, and metal salts, as shown below for ethylmagnesium iodide:



A similar reaction is given by ethylmagnesium bromide [73].

Thermal decomposition of organic compounds of aluminum such as  $\text{Al}(\text{C}_2\text{H}_5)_3$  takes place at temperatures around 600 °C with the formation of butenes,  $\text{C}_2\text{H}_4$ ,  $\text{H}_2$ , and aluminum. Low levels of  $\text{C}_2\text{H}_6$

were also generated in the process. Deposition of aluminum thin films was achieved by thermal decomposition above 40 °C of  $(\text{C}_2\text{H}_5)_3\text{AlH}_3$  (trimethylamine alane) [74,75].

Surface deposition of films of specific metals has been achieved, for example, for doping of specific surfaces as obtained with trimethylgallium decomposition on a silicon surface [2].

Germanium compounds are relatively similar to those of silicon. This can be seen, for example, in the decomposition of bis(alkoxyethynyl)-substituted germananes, which generate by decomposition ketenes, for example, (ethoxyethynyl)germanyl ketene, similar to the corresponding silane, while bis(alkoxyethynyl)-substituted stannanes decompose differently, generating a dimer type compound [15].

Tin (Sn) can exist in bivalent or quadrivalent state. The quadrivalent tin compounds are more stable to pyrolysis than those from divalent tin. For example, diethyl tin decomposes around 150 °C to form Sn and tetraethyl tin. Diphenyl tin generates tin and hexaphenyl distannane.

Pyrolysis of tetraethyl lead,  $\text{Pb}(\text{C}_2\text{H}_5)_4$ , has been reported [76], the compound generating free radicals  $\text{C}_2\text{H}_5$  at temperatures around its boiling point (200 °C). The formation of these free radicals has been used to increase the octane number of gasoline (see Section 7.1).

Other organic compounds of elements from the main groups of the periodic table, such as beryllium for the second group, indium and thallium for the third group, antimony and bismuth for the fifth group, selenium and tellurium for the sixth, have the properties of their organometallic compounds similar (to a certain extent) to that of the corresponding compounds of lighter elements, considering the increase in electropositive character of the element as the atomic number increases.

### Organometallic compounds of transitional elements

Zinc, cadmium, and particularly mercury have relatively stable organometallic compounds. Ethyl zinc, for example, can be obtained from ethyl zinc iodide by thermal decomposition at around 200 °C by the following reaction:



Dialkyl mercury compounds decompose generating hydrocarbons and Hg, and also char. The decomposition of diethyl mercury at 205 °C follows the main reaction shown below:



Asymmetrical alkyl mercury compounds suffer, at lower temperature, disproportionation reactions to form symmetrical compounds.

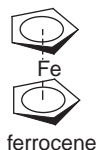
Diphenyl mercury decomposes above 300 °C to generate Hg,  $\text{C}_6\text{H}_6$ , biphenyl, and char. Monoalkyl mercury iodides generate by pyrolysis Hg,  $\text{HgI}_2$ , and hydrocarbons.

Other organometallic compounds are less stable. For example, thermal decomposition of  $\text{CH}_3\text{TiCl}_3$  and  $(\text{CH}_3)_2\text{TiCl}_2$  takes place slowly even at room temperature to generate  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_3\text{Cl}$ , 1,1,2-trichloropropene, etc. The reaction takes place by several competitive paths [77].

### Sandwich compounds

Chemical compounds containing a metal atom sandwiched between two arene units are known as sandwich compounds. The most common such compounds are the metallocenes, in which a metal atom such as Cr, Fe, Co, Ni, Zr, Ti, V, Mo, W, or Zn is sandwiched between two cyclopentadienyl rings. These compounds are also known as bis(cyclopentadienyl)metal. A few other sandwich compounds include bis(benzene)chromium, bis(cycloocta-tetraenyl)uranium, etc. Some mixed cyclopentadienyl compounds with only one cyclopentadiene cycle and another ligand on the other side of the molecule are also known. Pyrolysis of ferrocene or bis(cyclopentadienyl)iron,  $(\text{C}_5\text{H}_5)_2\text{Fe}$ , and other metallocenes became of considerable interest after the finding that pyrolysis of these compounds, or pyrolysis of

various alkanes in the presence of these compounds, leads to the formation of fullerenes and carbon nanotubes [78,79].



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## CHAPTER 23

*Toxicological and Environmental Aspects of Polycyclic Aromatic Hydrocarbons (PAHs) and Related Compounds***23.1. PAHs WITH TWO CONDENSED CYCLES*****General aspects***

The model compound in this class is naphthalene. Similar to polycyclic aromatic hydrocarbons (PAHs) with a larger number of aromatic cycles, naphthalene is considered a possible human carcinogen. Besides carcinogenicity, toxic effects are induced by high levels of naphthalene. In humans, these include hemolytic anemia, manifested by symptoms such as fatigue, lack of appetite, restlessness, and paleness. High levels of oral exposure to naphthalene also can cause nausea, vomiting, diarrhea, blood in the urine, and yellow skin. High-level exposures to naphthalene also can lead to cataract formation in laboratory animals and humans [1].

1-Methylnaphthalene and 2-methylnaphthalene were sometimes evaluated together with naphthalene regarding toxicity or carcinogenic potential [2]. Basically there are no differences regarding the toxicological effects between naphthalene and methylnaphthalenes.

**23.2. PAHs WITH MORE THAN TWO CYCLES*****General aspects***

For most PAHs, the main health-related concern is carcinogenicity. Many PAHs have been identified to cause tumors in laboratory animals, and epidemiological studies with people exposed to PAH mixtures for long periods of time have reported cancer development [3,4]. Other toxicological effects include reproductive, developmental, cardiovascular, bone marrow, liver, and immune toxicity. Most of the knowledge of PAH carcinogenicity in humans is based on occupational exposures [5]. Tumors are produced in lab animals by inhalation, dermal, or oral administration. Various agencies, including International Agency for Research on Cancer (IARC), National Toxicology Program (NTP), U.S. Environmental Protection Agency (EPA), American Conference of Governmental Industrial Hygienists (ACGIH), Occupational Safety and Health Administration (OSHA), Office of Environmental Health Hazard Assessment of the California Environmental Protection Agency (OEHHA), etc. have classified PAHs with respect to their carcinogenicity to animals or to humans.

***Classification of PAHs regarding carcinogenicity***

PAHs classification in different categories of carcinogens may be the same or may be different by different agencies (see Section 5.2). In IARC classification regarding carcinogenicity [6], PAHs are classified as known human carcinogen (Class 1), probable human carcinogens (Class 2A), possible human carcinogens (Class 2B), and not classifiable as carcinogens to humans (Class 3) (see Section 5.2). No PAH is classified as probably not carcinogenic to humans (Class 4). The IARC classification for a number of PAHs is given in Table 23.2.1.

The carcinogenicity of various compounds can be compared by using their carcinogenic potency  $TD_{50}$  (see Section 5.2) [7]. A relative potency can be calculated by taking the value  $1/TD_{50}$  for a standard compound as the unit. In the case of PAHs, the unit is usually taken for benzo[a]pyrene (BaP). Table 23.2.2 shows some examples of relative potency values for PAHs.

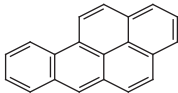
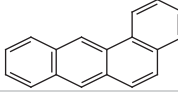
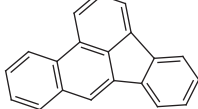
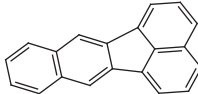
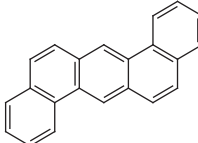
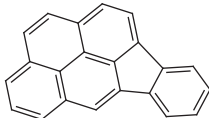
TABLE 23.2.1. IARC classification regarding carcinogenicity for a number of PAHs

No.	Compound	Class	No.	Compound	Class
1	Benzo[a]pyrene (BaP)	1	26	Benzo[ghi]fluoranthene	3
2	Dibenz[ah]anthracene	2A	27	Benzo[a]fluorene	3
3	Cyclopenta[cd]pyrene	2A	28	Benzo[b]fluorene	3
4	Dibenz[ah]anthracene	2A	29	Benzo[c]fluorene	3
5	Dibenzo[a]pyrene	2A	30	Benzo[ghi]perylene	3
6	Benzo[b]fluoranthene	2B	31	Coronene	3
7	Benzo[c]phenanthrene	2B	32	4H-Cyclopenta[def]chrysene	3
8	Benz[j]aceanthrylene	2B	33	5,6-Cyclopenteno-1,2-benzanthracene	3
9	Benzo[j]fluoranthene	2B	34	Dibenz[a]anthracene	3
10	Benzo[k]fluoranthene	2B	35	Dibenzo[ae]fluoranthene	3
11	Chrysene	2B	36	13H-Dibenzo[ag]fluorene	3
12	Dibenzo[ae]pyrene	2B	37	Dibenzo[ae]pyrene	3
13	Dibenzo[a]pyrene	2B	38	Dibenzo[e]pyrene	3
14	Indeno[1,2,3-cd]pyrene	2B	39	1,4-Dimethylphenanthrene	3
15	5-Methylchrysene	2B	40	1-Methylchrysene	3
16	Anthracene	3	41	2-Methylchrysene	3
17	Benzo[e]pyrene	3	42	3-Methylchrysene	3
18	Fluorene	3	43	4-Methylchrysene	3
19	Pyrene	3	44	6-Methylchrysene	3
20	Fluoranthene	3	45	2-Methylfluoranthene	3
21	Phenanthrene	3	46	3-Methylfluoranthene	3
22	Dibenzo[def,mno]chrysene (anthanthrene)	3	47	1-Methylphenanthrene	3
23	Benz[bc]aceanthrylene	3	48	Perylene	3
24	Benzo[b]chrysene	3	49	Picene	3
25	Benzo[a]fluoranthene	3	50	Pyrene	3

### BaP carcinogenicity

Among PAHs, BaP is considered to be a prototypical compound for the class. IARC classifies BaP as carcinogenic to humans based mostly on animal and mechanistic data. The EPA classifies BaP as a probable human carcinogen based on the fact that human data specifically linking BaP to a carcinogenic effect are lacking and the human data set is considered to be inadequate from EPA's standpoint. In humans, lung cancer has been shown to be induced by various mixtures of PAHs known to contain BaP, including cigarette smoke, roofing tar, and coke oven emissions. However, due to the fact that these agents are mixtures of PAHs and there are no controlled studies possible, it is not possible to conclude from these types of data that BaP is the only cancer-inducing agent. On the other hand, the evidence of carcinogenicity on BaP in animals is considered to be sufficiently strong. There are many animal studies in many species demonstrating that BaP is carcinogenic by multiple routes of administration. This evidence is supported by the fact that BaP also has produced positive results in numerous different genotoxicity assays (mammalian and nonmammalian systems). The animal carcinogenicity data on BaP include various administration routes (e.g., gavage, dietary, inhalation, intratracheal, dermal, subcutaneous), and these studies have been conducted in many strains of several species of rodents and primates. Repeated BaP administration has been associated with increased incidences of total tumors and with increased tumors at the sites of exposure and at distant sites (again, by various exposure routes). Because these types of studies are reproducible, BaP also has been used as a positive control for carcinogenicity studies.

TABLE 23.2.2. *Relative potency of some carcinogenic PAHs related to benzo[a]pyrene*

Compound	Structure	Abbreviation	Relative potency
Benzo[a]pyrene		BAP, BaP	1.0
Benz[a]anthracene		BAA, BaA	0.1
Benzo[b]fluoranthene		BBF, BbF	0.1
Benzo[k]fluoranthene		BKF, BkF	0.001
Dibenz[ah]anthracene		DBA	1.0
Indeno[1,2,3-cd]pyrene		IDP	0.1

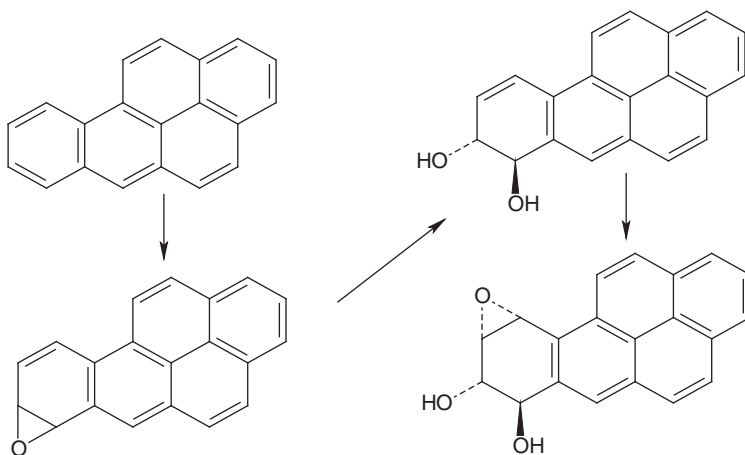
In animals, oral administration of BaP (e.g., via diet or gavage) to mice, rats, and hamsters has led to increased incidences of stomach tumors, dose dependently. Administration of BaP to rats indicated a statistically significant tendency toward formation of tumors of the forestomach, esophagus, and larynx dose dependently. Intratracheal instillation and inhalation administration of BaP to guinea pigs, hamsters, and rats has resulted in elevated incidences of respiratory tract and upper digestive tract tumors dose dependently [8]. Intraperitoneal BaP administration to rats and mice has produced increases in the number of tumors at the injection site [8,9]. Subcutaneous BaP administration to rats, mice, guinea pigs, hamsters, and primates have caused increases in the number of tumors at the injection site as well [10]. Because it is a reliable positive control, BaP often has been used as a positive control in many dermal studies, as its administration has been shown to produce skin tumors in rats, mice, rabbits, and guinea pigs, over a wide range of doses. BaP is a tumor initiator and a promoter (i.e., a complete carcinogen) in mouse skin carcinogenicity studies [10]. Even when administered dermally, BaP has been shown to lead to increased incidences of distant-site tumors in animals. BaP administration by other less common routes also has led to carcinogenicity in animals (e.g., intravenous, transplacental).

BaP has been shown to cause genotoxic effects in a many test systems [11]. For example, BaP was shown to be genotoxic in DNA damage assays and in reverse mutation and forward mutation assays. In mammalian cell culture, BaP was shown to be genotoxic in DNA damage, forward mutation, and chromosomal and cell transformation assays.

### ***The mechanism of PAH carcinogenicity***

The detailed evaluation of the mechanism of PAH carcinogenic effects is the subject of a large body of studies (see e.g. [12]), and a detailed presentation of this subject is beyond the purpose of this book.

Only some general concepts are further discussed. PAHs are in fact precarcinogens and do not appear to cause cancer without structural modifications. Three major pathways are considered responsible for the activation of precarcinogenic PAHs into carcinogenic metabolites, and they are (1) formation of diol-epoxides via cytochrome P450 enzymes, (2) formation of radical cations (via peroxidases), and (3) formation of reactive redox quinones via dihydrodiol dehydrogenases [11]. The formation of diol-epoxides is one of the main mechanisms of PAH carcinogenicity. In this mechanism, the PAH molecule is initially activated to a reactive intermediate by cytochrome P450 enzymes (e.g., CYP4501A1 and CYP4501B1). The primary function of these enzymes is to detoxify xenobiotics like PAHs by converting these lipophilic compounds into more water-soluble forms, and thus expediting excretion [13]. This process transforms PAH precarcinogens into proximate carcinogens and then into ultimate carcinogens. For the case of BaP, a 7,8-epoxide is initially formed by this mechanism involving CYP450 enzymes. Then the epoxide is transformed into a 7,8-diol by an epoxide hydrolase and further oxidated by a CYP450 enzyme to a 7,8-diol-9,10-epoxide. The main (simplified) activation path is shown as follows:



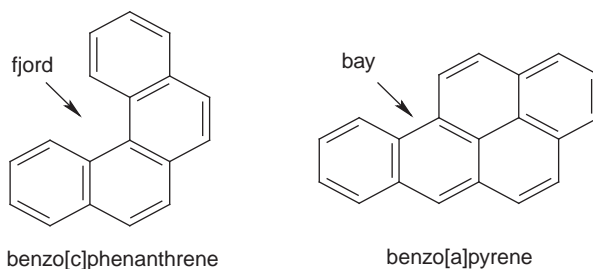
Upon formation of the ultimate carcinogenic metabolites, these reactive molecules interact with different cellular macromolecules (e.g., DNA, RNA, proteins), and, when the cellular controls are overcome, these interactions are implicated in the onset of cancer. The mechanism of carcinogenicity is complex, and a full discussion on the subject is beyond the scope of this book.

BaP metabolism has been studied in more detail compared to other members in the PAH class, and this compound is often cited in the literature as representative for the metabolism and effects of PAHs. In general, there are broad similarities between different PAH metabolism pathways. However, these similarities are, to some extent, only qualitative. Other PAHs form diol-epoxide metabolites, including benzo[*b*]-fluoranthene, chrysene, benzo[*a*]anthracene, 7,12-dimethylbenz[*a*]anthracene. Because of the different chemical structures and the resulting differences in physicochemical properties, the carcinogens have different specific structures, stabilities, and reactivity [14]. For example, the exact position of hydroxyl groups on the rings and the exact position of the epoxide differ for different compounds. For BaP, the reactive intermediate is 7,8-diol-9,10-epoxide, for benzo[*a*]anthracene, the reactive intermediate is 3,4-diol-1,2-epoxide [15]. Thus, the specific types and levels of metabolites formed are different for different parent compounds. In addition, there are target tissue and cell-type differences in the presence and types of various enzymes induced or used in the metabolism of PAHs [16–18].

While the formation of the 7,8-diol-9,10-epoxide in the case of BaP is thought to play a major role in the toxification pathway leading to carcinogenesis, other metabolic intermediates from BaP, benzo[*a*]anthracene, and 7,12-dimethylbenz[*a*]anthracene and other PAHs also can be mutagenic and are implicated in malignant transformations and carcinogenicity. These include the 7,8-diols, 9,10-diol-7,8-epoxides, 7,8- and 9,10-dihydro, and 7,8-catechol-metabolites [18].

Since considerable differences in the carcinogenic potential of PAHs has been noticed, numerous attempts were made to explain these differences. One theory developed for this purpose is related

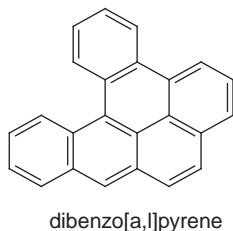
to the molecular geometry of each PAH, particularly to the presence of a “fjord” or “bay” region [19]. Two molecules from the PAH class, benzo[*c*]phenanthrene with a fjord and BaP with a bay are shown below:



It is hypothesized that in the bay area of a molecule, oxidation or radical formation can readily occur, while reactions involved in detoxification such as conjugation with glutathione or formation of glucuronides or sulfates are impeded [20]. Also, bay-region epoxides can undergo ring opening to form a carbonium ion much more easily than non-bay region epoxides [11]. This theory predicts that if a PAH can enzymatically form more than one diol-epoxide, then the one with its epoxide at the bay region will be the more biologically active among other diol-epoxide isomers and will bind cellular macromolecules. Higher propensity for formation of carbonium ions in the bay generally correlates with higher carcinogenic potential [17]. As a result, higher carcinogenicity is predicted for PAHs with a bay, and a lower one for the PAHs with a fjord.

This theory for prediction of carcinogenic potential of PAHs is not always applicable (presence of bay region may not necessarily lead to increased tumorigenic potential, and the presence of a fjord region is not a proof for the lack of carcinogenicity). An example of such exception is phenanthrene, which was predicted to be carcinogenic based on the presence of a bay region. Phenanthrene metabolizes to diol-epoxides, but the metabolites (1,2-; 3,4-; 9,10-dihydrodiols; and 1,2-diol-3,4-epoxide) show neither tumor-initiating activity in mouse skin painting nor lung tumors when injected in newborn mice. Other exceptions to the bay rule include benzo[*a*]anthracene, cyclopenta[*cd*]pyrene, and dibenzo[*ac*]anthracene [18].

The cases of molecules that contain both fjord and bay regions are more complex in terms of prediction of carcinogenic potential. One example is that of dibenzo[*a,l*]pyrene, which has both a bay and a fjord region. Dibenzo[*a,l*]pyrene has been demonstrated to be carcinogenic in experimental animals, having an even higher carcinogenic potency than BaP in some test systems (depending on the tests system and exposure conditions) [17]. The X-ray diffraction studies on dibenzo[*a,l*]pyrene showed that the molecule is not planar, presenting a 27.6° angle between the outermost rings and a widening of the C—C—C bond angles in the fjord region [21], which may explain (at least in part) the unexpected results.



### PAHs in the environment

The presence of PAHs in the environment can be natural or can be caused by human activities. PAHs occur naturally in fossil fuels such as coal, crude oil, coal-tar pitch, creosote, and asphalt. They are further transferred to numerous products made from these materials such as gasoline and other types

of combustibles. Industrial facilities that process fossil fuels such as coal gasification sites, and oil refineries may have elevated levels of PAHs. PAHs also are released into the air during the burning of fossil fuels, wood, garbage, or other organic substances. A higher level of PAHs is generated in the burning process when the burning is not efficient. Forest fires and volcanoes also produce PAHs naturally. A number of indoor household sources of PAHs are possible. These may include smoldering fireplaces, wood stoves, cigarette/tobacco smoke, unvented gas-burning appliances, kerosene heaters, and the charring or burning of food. Groundwater contaminated by gasoline or diesel fuel is another source for PAHs. Soil and groundwater contaminated with petroleum products, discharges from human activities such as industrial or domestic sewage effluents, runoff from paved roads and parking lots, offshore drilling, and leaching/disposal of refinery effluents may contain PAHs. A considerable number of studies are reported in the literature regarding distribution of PAHs in soil, water, atmosphere, etc. (see e.g., [22–25]).

### 23.3. PAHs WITH ADDITIONAL FUNCTIONALITIES

#### *General aspects*

Simple hydrocarbon PAHs are frequently associated with two other groups of polycyclic aromatic compounds. One group consists of PAHs that have functional groups attached to the aromatic rings. The most common compounds from this group are the nitro-PAHs and the hydroxy-PAHs. The second group consists of so-called aza-polycyclic aromatic hydrocarbons (aza-PAHs). The aza-PAHs are in fact heterocyclic compounds, and therefore they cannot be considered hydrocarbons. Among the heterocycles that were sometimes classified as aza-PAHs are acridines, carbazoles, other benzo-quinolines, and molecules with more condensed aromatic cycles containing heteroatoms. A discussion on pyrolysis of heterocyclic compounds can be found in Chapter 21, and aspects on their toxicity are discussed in Chapter 25.

#### *Nitro-PAHs*

The main source of nitro-PAHs is automobile emissions, particularly diesel exhaust (1-nitropyrene, 3-nitrofluoranthene, 8-nitrofluoranthene). Some industrial processes and residential heating also may generate nitro-PAHs. Some secondary sources of PAHs are possible, due to atmospheric or soil transformations of PAHs leading to the formation of several ambient nitro-PAHs (2-nitrofluoranthene, 1-nitropyrene, 2-nitropyrene). This process is the result of an initial reaction of PAHs with OH free radicals, followed by interaction with nitrogen oxides (NO<sub>2</sub>) also present in the environment. Although the exposure to nitro-PAHs is low, the mutagenic/carcinogenic character of these compounds is higher than that of the parent (hydrocarbon) compound [26].

The list of nitro-PAHs recognized by IARC as known, probable, or possible human carcinogens includes 5-nitroacenaphthene, 6-nitrochrysene, 2-nitrofluorene, 1-nitropyrene, and 4-nitropyrene.

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## CHAPTER 24

*Toxicological and Environmental Aspects of Dioxin-Like Compounds***24.1. HALOGENATED AROMATIC HYDROCARBONS (PCBs AND PBBs)****General aspects**

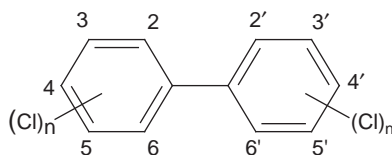
Dioxin-like compounds (DLCs) include basically three classes of compounds: (poly)chlorinated biphenyls, (poly)chlorinated dibenzo-*p*-dioxins, and (poly)chlorinated dibenzofurans. The levels of DLC estimated to be released to the air, land, and water in the United States from different sources in 1987, 1995, and 2000 are given in Table 24.1.1 [1].

As shown in Table 24.1.1, a considerable decrease of approximately 90% in the level of the environmental releases of DLCs was achieved between 1987 and 2000. This was possible through a combination of regulatory activities, improved emission controls, voluntary actions on behalf of industry, and the closing of a number of facilities. However, the main sources of DLCs remained the activities related to burning. For this reason, the study of generation of DLCs in pyrolytic processes is very important.

Besides the chlorinated compounds, the brominated analogs are also part of this class. While chlorine is more common in nature than bromine, it is also more frequently used in industrial processes. The use of brominated flame retardants increased the presence of brominated DLC in the surrounding medium. Some of the DLC compounds are strong carcinogens, highly toxic substances, and persistent pollutants with high propensity of bioaccumulation. For these reasons, their generation by intended or unintended pyrolytic processes is under considerable attention [2–4].

**Halogenated biphenyls**

Polychlorinated biphenyls (PCBs) are compounds of particular interest regarding toxicological aspects. The compounds from this class have the following general formula:



The PCBs may contain 1–10 chlorines in the molecule. Although they were banned for production in the 1970s and phased out in the 1980s, they were produced industrially in the past for various purposes. Since PCBs are generated in different pyrolysis processes including waste incineration, they are still of significant human health concern. In addition, PCBs and polybrominated biphenyls (PBBs) are of concern to the environment, as these types of compounds are known to be directly and indirectly toxic to animal life. In water, PCBs can be toxic to aquatic species. In turn, aquatic species are eaten by birds or mammals, PCBs accumulate in fatty tissues, and their concentration increases, increasing toxicity for the end species, a phenomenon known as biomagnification. They are classified as persistent organic pollutants with low biodegradability and high bioaccumulation characteristics due to their lipophilic nature.

PCBs tend to have dioxin-like properties, but their toxicity varies considerably among congeners. The coplanar PCBs known as non-*ortho* PCBs are among the most toxic ones. The planar structure is associated with the lack of Cl atoms in *ortho* positions of the biphenyl rings.

Oral, inhalation, and dermal exposures are the main routes of concern in humans. In humans, PCB exposure to high levels can lead to chloracne, skin rashes, vesicular eruptions, and transient liver



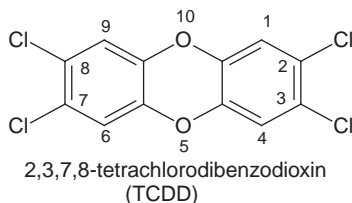
TABLE 24.1.1. *The levels of DLC (in g and percent contribution) from the top ten sources in 1987, 1995, and 2000 estimated to be released to the air, land, and water in the United States [1]*

Rank	1987			1995			2000		
	Source	Amount (g)	Total (%)	Source	Amount (g)	Total (%)	Source	Amount (g)	Total (%)
1	Municipal waste combustion	8905	63.80	Municipal waste combustion	1394	40.50	Outdoor trash burning	498.5	35.10
2	Medical waste incineration	2570	18.40	Outdoor trash burning	628	18.20	Medical waste incineration	378	26.60
3	Secondary copper smelting	983	7.00	Medical waste incineration	487	14.10	Municipal wastewater treatment sludge	89.7	6.30
4	Outdoor trash burning	604	4.30	Secondary copper smelting	271	7.90	Municipal waste combustion	83.8	5.90
5	Bleached pulp and paper mills	370	2.60	Cement kilns	156	4.50	Coal-fired utility boilers	69.5	4.90
6	Cement kilns	118	0.80	Municipal wastewater treatment sludge	133	3.90	Diesel heavy-duty trucks	65.4	4.60
7	Municipal wastewater treatment sludge	85	0.60	Coal-fired utility boilers	60	1.70	Industrial wood combustion	41.5	2.90
8	Coal-fired utility boilers	51	0.40	Vinyl/ethylene chloride production	36	1.00	Diesel off-road equipment	33.1	2.30
9	Automobiles using leaded gasoline	38	0.30	Diesel heavy-duty trucks	33	1.00	Vinyl/ethylene chloride production	30	2.10
10	2,4-Dichloro-phenoxy-acetic acid	33	0.20	Bleached pulp and paper mills	30	0.90	Sintering plants	27.6	1.90
	Other	208	1.50	Other	216	6.30	Other	104.9	7.40
	Total	13,965	100	Total	3444	100	Total	1422	100

alterations (e.g., changes in liver enzymes). Typically, chloracne can be the only manifestation of toxicity. Chloracne onsets about 1–3 weeks after exposure and can result from exposure via inhalation, dermal, or oral routes [5]. The immune, reproductive, developmental, endocrine, and nervous systems are additional targets of toxicity in both animals and humans.

Some studies on humans with chronic PCB exposure showed association with specific kinds of cancer, such as cancer of the liver and biliary tract. The EPA and IARC have determined that PCBs are probably carcinogenic to humans. Examples of PCBs listed on IARC as 2A (probable human carcinogens) include the following 1,1'-biphenyls: 2-chloro-, 4-chloro-, 2,2'-dichloro-, 2,3'-dichloro-, 2,4'-dichloro-, 4,4'-dichloro-, 2,2',3-trichloro-, 2,2',5-trichloro-, 2,3',4-trichloro-, 2',3,4-trichloro-, 2,4,4'-trichloro-, 2,4',5-trichloro-, 2,2',3,5'-tetrachloro-, 2,2',4,5'-tetrachloro-, 2,2',5,5'-tetrachloro-, 2,3,4,4'-tetrachloro-, 2,3',4,4'-tetrachloro-, 2,3',4',5-tetrachloro-, 3,3',4,4'-tetrachloro-, 2,2',3,3',6-pentachloro-, 2,2',3,4,5'-pentachloro-, 2,2',3',4,5-pentachloro-, 2,2',3,4',6-pentachloro-, 2,2',3,5',6-pentachloro-, 2,2',4,4',5-pentachloro-, 2,2',4,5,5'-pentachloro-, 2,3,3',4,4'-pentachloro-, 2,3,3',4',6-pentachloro-, 2,3',4,4',5-pentachloro-, 2,2',3,3',4,6-hexachloro-, 2,2',3,3',6,6'-hexachloro-, 2,2',3,4,4',5-hexachloro-, 2,2',3,4,4',5'-hexachloro-, 2,2',3',4,5,6'-hexachloro-, 2,2',4,4',5,5'-hexachloro-, 2,2',3,3',4,4',5-heptachloro-, 2,2',3,3',4,5,6'-heptachloro-, and 2,2',3,4,4',5,5'-heptachloro-1,1'-biphenyl.

PCBs are seldom encountered in the environment as a unique chemical compound. Mixtures of PCBs and frequently dioxins and furans are commonly present together. In an attempt to address various practical issues, the World Health Organization has developed a method that allows for determination of the toxicity ranking of various related structures (most often dioxin or dioxin related) in a chemical mixture. The method is used in risk assessment and is based on calculating toxicity equivalent quotients (TEQ), also known as toxicity equivalents. TEQ is defined as the contribution of specified component(s) to the toxicity of a mixture of related substances (e.g., chlorinated dibenzo-*p*-dioxins, furans, and biphenyls). The amount (or concentration) of substance of total toxicity equivalent is the sum of that for the components. Within the TEQ method, each dioxin type compound is assigned a toxic equivalency factor (TEF). Most often, this factor denotes a given dioxin or dioxin-related compound toxicity relative to 2,3,7,8-tetrachloro-dibenzodioxin (TCDD), which is assigned the maximum toxicity designation of 1 ( $\text{TEF}_{\text{TCDD}} = 1$ ). Other dioxin compounds are given equal or lower numbers, with each number roughly proportional to its toxicity relative to that of TCDD. The mixture toxicity is calculated as follows:



$$\text{TEQ}_{\text{mixture}} = \sum C_n \times (\text{TEF})_n \quad (24.1.1)$$

where  $C_n$  is the concentration (or mass) of the individual congener in the complex mixture.

Examples of TEFs for several PCBs are given in Table 24.1.2. As seen from this table, among PCBs, 3,3',4,4',5-pentachlorobiphenyl (PCB 126) has the highest TEF and is the most toxic relative to TCDD in this mixture.

The structure of PCBs plays an important role in determining the TEF value. The presence of voluminous substituents in positions 2,6 and 2',6' that lead to a nonplanar structure of the molecule of PCB is typically associated with a low TEF. Higher TEF values are seen for PCBs with a planar structure that have hydrogen atoms in positions 2,6 and 2',6'.

Bearing similarity in toxicological profile to PCBs, PBBs induce immunotoxicity in animals. In humans, PBBs may cause skin problems, such as acne. Studies on animals exposed to large amounts of PBBs for a short period or to smaller amounts over a longer period of time show that PBBs can cause weight loss, skin disorders, nervous and immune systems effects, as well as effects on the liver, kidneys, and thyroid gland. A considerable volume of additional information regarding PCBs is available in the literature [9].

TABLE 24.1.2. *The toxic equivalence factors (TEF) for various PCBs as reported by World Health Organization (WHO) [6–8]*

PCB IUPAC no.	Congener structure	TEF		
		WHO 1994 [6]	WHO 1997 [7]	WHO 2005 [8]
77	3,3',4,4'-Tetrachlorobenzene	0.0005	0.0001	0.0001
81	3,4',4',5-Tetrachlorobenzene	–	0.0001	0.0003
105	2,3,3',4,4'-Pentachlorobenzene	0.0001	0.0001	0.00003
114	2,3,4,4',5-Pentachlorobenzene	0.0005	0.0005	0.00003
118	2,3',4,4',5-Pentachlorobenzene	0.0001	0.0001	0.00003
123	2',3,4,4',5-Pentachlorobenzene	0.0001	0.0001	0.00003
126	3,3',4,4',5-Pentachlorobenzene	0.1	0.1	0.1
156	2,3,3',4,4',5-Hexachlorobenzene	0.0005	0.0005	0.00003
157	2,3,3',4,4',5'-Hexachlorobenzene	0.0005	0.0005	0.00003
167	2,3',4,4',5,5'-Hexachlorobenzene	0.00001	0.00001	0.00003
169	3,3',4,4',5,5'-Hexachlorobenzene	0.01	0.01	0.03
170	2,2',3,3',4,4',5-Heptachlorobenzene	0.0001	–	–
180	2,2',3,4,4',5,5'-Heptachlorobenzene	0.00001	–	–
189	2,3,3',4,4',5,5'-Heptachlorobenzene	0.0001	0.0001	0.00003

## 24.2. HALOGENATED DIBENZO-*p*-DIOXINS AND DIBENZOFURANS

### General aspects

The toxic effects of chlorinated dibenzodioxins (dioxins or PCDDs or CDDs), chlorinated dibenzofurans (furans or PCDFs or CDFs), and other DLCs (coplanar PCBs) include lethal effects on specific animals at levels ranging from 1 µg/kg body weight to 5000 µg/kg body weight; immune system damage (at similar levels) because of damage to the thymus gland causing changes in cell immunity (likely to have similar effect on children); damage to organs such as liver, kidney, and digestive tract; reproductive effects including miscarriage and sterility, possible birth defects (particularly neurological); cancer (TCDD has been classified as a proven human carcinogen, evidence of some tumor initiation, verified animal carcinogen); and persistent skin eruptions in humans and some animals (chloracne) [10]. For these reasons, the levels of DLCs are of considerable concern.

Similar to the case of PCBs, various CDDs and CDFs are classified based on their toxicity equivalents with TCDD. The TEQ values are reevaluated periodically, as more experimental results are accumulated for each individual compound. The toxic equivalence factors (TEF) for various CDDs as reported by World Health Organization in 1998 and revised in 2005 are indicated in Table 24.2.1, and the values for TEF of various CDFs are given in Table 24.2.2 [11].

There are three main mechanisms that act together and determine the emission of CDDs and CDFs from burning sources [12,13]. The first mechanism (referred to as “pass through” or “transfer”) consists of the release during burning of some of the preexistent CDDs and CDFs that were present as contaminants in the combusted organic material. Depending on the material that burns and the burning procedure, the destruction of the preexistent CDDs and CDFs and therefore the release of the remaining part of these compounds vary considerably. A large body of literature is available regarding the presence of DLCs in specific materials (see, e.g., [14,3,15]), specific locations (see, e.g., [16]), processing facilities (see, e.g., [17]), etc.

The second mechanism (referred to as “precursor”) consists of the formation of CDDs and CDFs from the thermal breakdown and molecular rearrangement of precursor ring compounds, such as chlorinated aromatic hydrocarbons, phenols, and other compounds that have a structural resemblance to the CDDs and CDFs molecules.

The third mechanism (referred to as “de novo” synthesis) is similar to the precursor mechanism, but the precursor compounds are not necessarily aromatic or chlorinated molecules, and they are a result of

TABLE 24.2.1. *The toxic equivalence factors (TEF) for various CDDs as reported by World Health Organization (WHO) [2]*

Compound	Notation	WHO 1998	WHO 2005
2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin	2,3,7,8-TCDD	1	1
1,2,3,7,8-Pentachlorodibenzo- <i>p</i> -dioxin	1,2,3,7,8-PeCDD	1	1
1,2,3,4,7,8-Hexachlorodibenzo- <i>p</i> -dioxin	1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-Hexachlorodibenzo- <i>p</i> -dioxin	1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-Hexachlorodibenzo- <i>p</i> -dioxin	1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-Heptachlorodibenzo- <i>p</i> -dioxin	1,2,3,4,6,7,8-HpCDD	0.01	0.01
Octachlorodibenzo- <i>p</i> -dioxin	OCDD	0.0001	0.0003

TABLE 24.2.2. *The toxic equivalence factors (TEF) for various CDFs as reported by World Health Organization (WHO) [2]*

Compound	Notation	WHO 1998	WHO 2005
2,3,7,8-Tetrachlorodibenzofuran	2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-Pentachlorodibenzofuran	1,2,3,7,8-PeCDF	0.05	0.03
2,3,4,7,8-Pentachlorodibenzofuran	2,3,4,7,8-PeCDF	0.5	0.3
1,2,3,4,7,8-Hexachlorodibenzofuran	1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-Hexachlorodibenzofuran	1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-Hexachlorodibenzofuran	1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-Hexachlorodibenzofuran	2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-Heptachlorodibenzofuran	1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-Heptachlorodibenzofuran	1,2,3,4,7,8,9-HpCDF	0.01	0.01
Octachlorodibenzofuran	OCDF	0.0001	0.0003

heterogeneous reactions on fly ash (particulate matter) involving carbon, oxygen, hydrogen, organic and inorganic chlorine, and a transition metal catalyst [18,19]. Although chlorine is an essential component for the formation of CDDs and CDFs in combustion systems, the empirical evidence indicates that for commercial-scale incinerators, chlorine levels in feed are not the dominant controlling factor for rates of CDDs and CDFs in stack emissions [20]. Particulate-bound carbon is suggested as the primary reagent in the “de novo” synthesis pathway. Incomplete combustion plays a critical role in the initial formation of simple aromatic molecules that later evolve into complex aromatic precursors. CDDs and CDFs are formed from the intermediate compounds by the contribution of free chlorine atoms ubiquitous in burning materials. For commercial-scale incinerators, by both the second and the third mechanism, the formation of CDDs and CDFs occurs outside the furnace, in the so-called post-combustion zone. In fact, there is no clear distinction between the precursor and the “de novo” synthesis mechanisms of CDD and CDF formation. Both formation pathways depend on the generation of precursors within combustion gases, the interaction of reactive fly ashes, a generally oxidative environment, the presence of a transition metal catalyst, the presence of gaseous chlorine, and a favorable range of temperature. The temperature of the combustion gases (i.e., flue gases) is the single most important factor in forming DLCs. Temperatures between 200 °C and 450 °C are most conducive to the formation of CDDs and CDFs, with maximum formation occurring at around 350 °C. If the temperature falls outside this range, the amount of CDDs/CDFs formed is minimized. This variation in the level of CDDs and CDFs with temperature in the carbon/fly ash system in a furnace is shown in Figure 24.2.1 [21,22].

Besides chlorinated compounds previously listed, a number of brominated dibenzodioxins and dibenzofurans are also of concern [23]. These compounds are of increased concern due to the

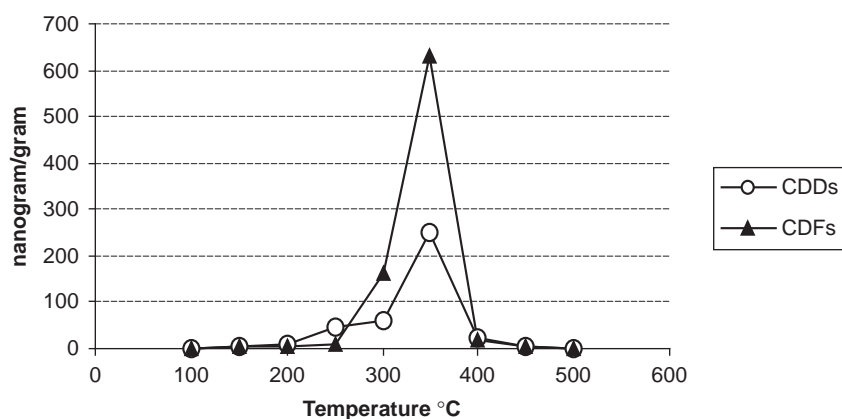


FIGURE 24.2.1. Variation in the level of CDDs and CDFs with temperature in the carbon/fly ash system in a furnace [22].

widespread use of brominated flame retardants. Basically, the mechanism of formation of these compounds is similar to the formation of chlorinated DLCs.

Similar to the case of PCBs, a considerable volume of additional information regarding CDDs and CDFs is available in the literature [9].

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## CHAPTER 25

*Toxicological Aspects of Aromatic Heterocyclic Amines***25.1. HETEROCYCLIC AROMATIC AMINES****General aspects**

A number of heterocyclic aromatic amines (HAAs) are formed by pyrolytic processes particularly from amino acids in pure form, but also from amino acids and other nitrogenous compounds in interaction with sugars and creatinine. HAAs are also generated by pyrolysis from more complex mixtures containing nitrogenous materials like proteins, but without the possibility to determine the precise origin of the HAAs. Since HAAs are mutagenic and suspected carcinogens in humans, and because amino acids and sugars are common in food, the presence of HAAs in food is of particular concern. Some aspects regarding the formation of aromatic heterocyclic amines were discussed in Sections 13.5, 18.1, and 21.2. A considerable amount of information on the presence of HAAs in food, smoke, and environment is reported in the literature [1–31]. The information is also summarized in excellent reviews [27,32–35] and in at least one monograph [36].

Several studies were focused on mutagenic properties of HAAs [32]. These compounds are generated in food when it is cooked at temperatures over 150 °C. The range of HAAs levels is between 0.1 ppb and 50 ppb, depending on the food and cooking conditions. The HAAs are not only present in cooked red meat, fish, and chicken, but also at lower levels in baked and fried foods derived from grain. Mutagenicity of fried beef hamburgers cooked at 230 °C was determined to be  $800 \pm 37$  TA98 revertants per gram of cooked material [32] in the Ames/Salmonella test. In the tested fried beef, the reported level of 2-amino-3,8-dimethyl-imidazo[4,5-*f*]quinoxaline (MeIQx) was  $3.0 \pm 2.0$  ng/g, of 2-amino-3,4,8-trimethyl-imidazo[4,5-*f*]quinoxaline (DiMeIQx) was  $1.0 \pm 0.18$  ng/g, of 2-amino-3-methyl-imidazo[4,5-*f*]quinoline (IQ) was  $0.06 \pm 0.03$  ng/g, and of 2-amino-1-methyl-6-phenylimidazo[4,5-*b*]pyridine (PhIP) was 9.6 ng/g. HAAs were capable of producing both reverse and forward mutations in *Salmonella* bacteria and forward mutations in Chinese hamster ovary cells (CHO). The number and type of mutations depended on the repair capacity of the cells for both *Salmonella* and CHO. Also, there were statistically significant increases in the mutations in the pancreas of the “mutamouse” following PhIP exposure.

Based on findings from studies on multiple species of experimental animals it was shown that heterocyclic amines produced cancer in multiple organs including forestomach, cecum, colon, liver, oral cavity, Zymbal gland, mammary gland, and skin. Although evidence from human epidemiology suggests that consumption of well-done or grilled meat (which may contain HAAs) may be associated with increased cancer risk, the data are insufficient to support the conclusion that this risk is due specifically to certain HAAs present in these foods.

The list of some heterocyclic amines (including two heterocyclic compounds, harman, and norharman) together with their most common origin is given in Table 25.1.1.

The list of detected HAAs is not limited to those listed in Table 25.1.1. Other similar compounds, such as tetrahydro- $\beta$ -carbolines [37] were reported in specific samples.

Studies on HAAs were also directed toward the measuring of certain markers of exposure to these compounds [38]. For example, after ingestion by different animals, only a few percent of the initial levels of MeIQx and PhIP were excreted as parent compounds. It was determined that urinary levels of parent HAA reflect only recent exposure. The excreted glucuronide conjugates of N-hydroxy-PhIP and N-hydroxy-MeIQx could be markers for the N-hydroxylation capacity and HAA exposure. 5-OH-PhIP can be considered a metabolite marker for PhIP, since it is formed from this compound as a by-product along with the formation of PhIP-DNA adducts. PhIP also gives adducts of serum albumin and hemoglobin. In mice, PhIP is irreversibly incorporated in a dose-dependent manner into hair. In humans exposed to an ordinary diet it was found that the level of PhIP can vary from <50–5000 pg PhIP/g hair.

TABLE 25.1.1. *Heterocyclic amines of health concern and their most likely source following pyrolysis*

Acronym	Compound	Likely pyrolytic origin	Reference
A $\alpha$ C	2-Amino-9H-pyrido[2,3- <i>b</i> ]indole	Soybean globulin	1, 5, 6, 16, 19, 20
4-CH <sub>2</sub> OH-8-MeIQx	2-Amino-4-hydroxymethyl-3,8-dimethylimidazo[4,5- <i>f</i> ]-quinoxaline		16–18, 26
Cre-P-1	4-Amino-1,6-dimethyl-2-methylamino-1H,6H-pyrrolo[3,4- <i>f</i> ]benzimidazol-2,5,7-dione	Proteins	27
4,8-DiMeIQx	2-Amino-3,4,8-trimethylimidazo[4,5- <i>f</i> ]quinoxaline	Fried beef	27
7,8-DiMeIQx	2-Amino-3,7,8-trimethylimidazo[4,5- <i>f</i> ]quinoxaline		27
7,9-DiMeIQx	2-Amino-1,7,9-trimethylimidazo[4,5- <i>f</i> ]quinoxaline		27
1,6-DMIP	2-Amino-1,6-dimethylimidazo[4,5- <i>b</i> ]pyridine		27
Glu-P-1	2-Amino-6-methyldipyrro[1,2- <i>a</i> :3',2'- <i>d</i> ]imidazole	Glutamic acid	10, 13–15, 18
Glu-P-2	2-Aminodipyrro[1,2- <i>a</i> :3'2'- <i>d</i> ]imidazole	Glutamic acid	10, 13–15
Harman	1-Methyl-9H-pyrido[3,4- <i>b</i> ]indole	Coffee	20, 23, 24
IFP	2-Amino-1,6-dimethylfuro[3,2- <i>e</i> ]imidazo[4,5- <i>b</i> ]pyridine		22, 27
IQ	2-Amino-3-methylimidazo[4,5- <i>f</i> ]quinoline	Broiled sardines	10, 25
IQx	2-Amino-3-methylimidazo[4,5- <i>f</i> ]quinoxaline		21, 28
Lys-P-1	3,4-Cyclopentenopyrido[3,2- <i>a</i> ]carbazole	Lysine	27
MeA $\alpha$ C	2-Amino-3-methyl-9H-pyrido[2,3- <i>b</i> ]indole	Soybean globulin	1, 5, 6, 10, 16
MeIQ	2-Amino-3,4-dimethylimidazo[4,5- <i>f</i> ]quinoline	Broiled sardines	18
8-MeIQx	2-Amino-3,8-dimethylimidazo[4,5- <i>f</i> ]quinoxaline	Fried beef	1, 18, 22, 25, 26
4-MeIQx	2-Amino-3,4-dimethylimidazo[4,5- <i>f</i> ]quinoxaline	Fried beef	1, 18, 22, 25, 26
	1-Methyl-6-phenylimidazo[4,5- <i>b</i> ]pyridine-2-ylamine	Alanine?	27
Norharman	9H-Pyrido[3,4- <i>b</i> ]indole	Coffee	13, 15, 20, 23, 24
Orn-P-1	4-Amino-6-methyl-1H-2,5,10,10b-tetraaza-fluoranthene	Ornithine	27
4'OH-PhIP	2-Amino-1-methyl-6-(4-hydroxyphenyl)imidazo[4,5- <i>b</i> ]pyridine		27
Phe-P-1	2-Amino-5-phenylpyridine	Phenylalanine	2, 27
PhIP	2-Amino-1-methyl-6-phenylimidazo[4,5- <i>b</i> ]pyridine	Smoke	11, 19, 22, 25
1,5,6-TMIP	2-Amino-1,5,6-trimethylimidazo[4,5- <i>b</i> ]pyridine		27
Trp-P-1	3-Amino-1,4-dimethyl-5H-pyrido[4,3- <i>b</i> ]indole	Tryptophan	1, 2, 5–7
Trp-P-2	3-Amino-1-methyl-5H-pyrido[4,3- <i>b</i> ]indole	Tryptophan	2, 5–7, 10
TriMeIQx	2-Amino-3,4,7,8-tetramethylimidazo[4,5- <i>f</i> ]quinoxaline		27

It was suggested that this measurement could provide an indication of the level of exposure to PhIP [38].

Other studies attempted to find the metabolic path of HAAs [28,39]. It is likely that the first step in metabolic activation of mutagenic and carcinogenic heterocyclic amines is N-hydroxylation by cytochrome P-448. N-hydroxyamino compounds are further activated to form N-O-acyl derivatives that readily react with DNA. The adducts between the metabolites of Trp-P-2 and Glu-P-1, and DNA were shown to have a C8-guanylamino structure [39]. In the case of Glu-P-1, modification of guanine in GC clusters occurs preferentially. It was shown also that glutathione transferases and myeloperoxidase inactivated some heterocyclic amines or their active metabolites [39]. Also, hemin and fatty acids bind to HAAs and inactivate them. Fibers and other factors from vegetables also work to inactivate heterocyclic amines. Nitrite at low pH degraded some heterocyclic amines, but those with an imidazole moiety were found to be resistant. Glu-P-1 induced intestinal tumors in a high incidence when fed orally to rats.



When  $^{14}\text{C}$ -Glu-P-1 was administered by gavage into rats, about 50% and 35% were excreted into feces and urine, respectively, within 24 h. When the bile was collected, around 60% of radioactivity was found excreted into it within 24 h. In the bile, N-acetyl-Glu-P-1 was identified as one of the metabolites of Glu-P-1 [39].

In a different study [40], the metabolic activation of IQ to mutagenic intermediates in the Ames test was studied with hepatic activation systems from control and IQ-treated rats. Hepatic S9 preparations from IQ-treated rats were more efficient than the control in converting IQ to mutagens. An increase was seen also when isolated microsomes were employed as activation systems, but this was less pronounced. The microsome-mediated mutagenicity of IQ was potentiated by addition of the cytosolic fraction from control and IQ-treated rats, the latter being more effective. It was concluded that IQ, at the doses employed in the study, enhances its own bioactivation to genotoxic metabolites by stimulating both its microsomal and cytosolic metabolism.

Several theoretical studies were performed with the aim to correlate physicochemical characteristics of HAAs with their carcinogenic properties [41,42]. In one of these studies [42], 11 possible 2-amino-trimethylimidazopyridine isomers were tested for mutagenic potency in the Ames/Salmonella test with bacterial strain TA98. These compounds are related to those found in heated muscle meats. Structural, quantum chemical, and hydropathic data were calculated on the parent molecules and the corresponding nitrenium ions. The principal determinants of higher mutagenic potency in these amines were indicated to be: (1) a small dipole moment, (2) the combination of *b*-face ring fusion and N3-methyl group, (3) a lower calculated energy of the  $\pi$  electron system, (4) a smaller energy gap between the amine HOMO and LUMO orbitals (Pearson "softness") (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital), and (5) a more stable nitrenium ion.

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